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NAME OF AUTHOR/*NOM DE L'AUTEUR* Dusko Jericevic

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NAME OF SUPERVISOR/*NOM DU DIRECTEUR DE THÈSE* Dr. M. Le Maguer & Dr. P. Jelen

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THE UNIVERSITY OF ALBERTA

REHYDRATION AND SORPTION PROPERTIES OF POTATO GRANULES

by

DUSKO JERICEVIC

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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DATED ..... Dec. 11 1975

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled 'REHYDRATION AND SORPTION PROPERTIES OF POTATO GRANULES' submitted by DUSKO JERICEVIĆ in partial fulfilment of the requirements for the degree of Master of Science

.....
Supervisor

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DATE.....Dec 11.....1975

ABSTRACT

The cause of the inconsistent rehydration rate of freeze-thaw potato granules was investigated. The first part of the investigation involved a study of the outer surface of the granules by scanning electron microscopy. The difference between potato cells and granules was established and the causes of the formation of aggregates of potato cells are discussed. The outer surface of the granules does not seem to have an influence upon the rehydration properties of potato granules: the aggregation of potato cells results in formation of fissures through which water penetrates freely into the interior of the granules but not through the cell wall.

Adsorption-desorption properties of potato granules were studied to determine the porosity and pore size distribution of the potato cells. It was found that the majority of the pores is too small to allow water to penetrate through them.

The relationships between diffusion coefficients and the initial moisture content of the granules was determined. The results show the independency of the initial moisture content on diffusivity of the granules. This suggests that the main transport of water into the cells occurs through the solid phase.

Further study showed that the variability in initial moisture content of the granules and also the internal molecular rearrangement of the granules upon storage might influence the changes of rehydration properties of potato granules.

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TABLE OF CONTENTS

		Page
INTRODUCTION		1
CHAPTER 1.	REVIEW OF THE LITERATURE	5
	1.1. Processing of Potato Granules	5
	1.2. Effect of Processing on Potato Cell Separation	9
	1.2.1. Potato cell structure	9
	1.2.2. Selection of potatoes for processing	10
	1.2.3. Cooking	11
	1.2.4. Mashing	11
	1.2.5. Freezing, thawing and granulation	12
	1.3. Potato Starch and its Characteristics Related to the Potato Granules	13
	1.3.1. Generally on starch	13
	1.3.2. Water effect	14
	1.3.3. Heat effect	15
	1.3.4. Retrogradation	16
	1.3.5. Effect of surfactants	17
	1.3.6. Modification	17
	1.4. Starch and its Influence on Dough Formation	18
CHAPTER 2.	OBJECTIVES OF THE INVESTIGATIONS	22
CHAPTER 3.	MATERIALS AND PREPARATIONS OF MATERIALS	25
	3.1. Raw Potatoes	25
	3.2. Preparation of Potato Starch from Raw Potato	25
	3.3. Potato Granules	26
	3.3.1. Processing of potato granules with the aid of freeze-thaw technique	26

TABLE OF CONTENTS CONTINUED

	Page
3.3.2. Add-back process potato granules and french fry mix.....	27
3.3.3. Bulk density determination of the granules.....	27
3.3.4. Potato dough and freeze dried reconstituted potato granules.....	27
3.3.4.1. Preparation of the potato dough from potato granules.	27
3.3.4.2. Preparation of the freeze dried reconstituted potato granules.....	28
CHAPTER 4. OUTER SURFACE OF POTATO GRANULES.....	29
4.1. Introduction to Scanning Electron Microscopy (SEM).....	29
4.2. Application of SEM to Potato Granules.....	32
4.2.1. Method.....	32
4.2.2. Introduction.....	33
4.2.3. The formation of aggregates. Pore volume.....	35
4.2.4. External and internal surface. Fissures.....	37
4.2.5. Porous structure.....	42
4.2.6. Size and shape of granules and bulk density.....	52
4.2.7. Remarks.....	55
CHAPTER 5. INNER SURFACE OF POTATO GRANULES. PORE SIZE. AND PORE SIZE DISTRIBUTION.....	58
5.1. Sorption Characteristics and Related Physical Properties.....	58
5.1.1. Theory of Sorption.....	58
5.1.2. The BET theory. Equation and model assumptions.....	60
5.1.3. Practical use and limitations.....	61
5.2. Capillarity.....	63
5.2.1. The Kelvin equation, assumptions and concept of critical radius (R_c) and thickness of adsorbed layer (t).	63

TABLE OF CONTENTS CONTINUED

	Page
5.2.2. Different types of pores.....	66
5.2.3. Calculation of pore size distribution.....	67
5.3. Application to Potato Granules.....	69
5.3.1. Methods.....	69
5.3.1.1. Water activity.....	69
5.3.1.2. Moisture content.....	70
5.3.1.3. Sorption isotherms. Monolayer capacity. Heat of adsorption.....	70
5.3.1.4. Pore size distribution (PDT).....	71
5.3.2. Results and discussion of results...	72
5.3.3. Remarks.....	79
CHAPTER 6. REHYDRATION STUDIES.....	81
6.1. Introduction.....	81
6.2. Theory of Diffusion.....	81
6.3. Boundary Conditions. Mass Transfer Resistance at the Surface.....	84
6.4. Application to Potato Granules.....	84
6.4.1. Introduction.....	84
6.4.2. Methods.....	85
6.4.2.1. Determination of diffusion coefficient.....	85
6.4.2.2. Determination of rehydration rate of potato granules.....	87
6.4.2.3. Structural rearrangement as analyzed by differential thermal analysis (DTA).....	88
6.4.3. Results.....	89
6.4.3.1. Effect of water content of the granules on diffusivity	89

TABLE OF CONTENTS CONTINUED

	Page
6.4.3.2. Effect of uncontrolled atmosphere on rehydration of the granules.....	95
6.4.3.3. Effect of controlled atmosphere on rehydration of the granules.....	100
6.4.3.4. Effect of storage on rehydration of the granules.....	110
6.4.3.5. Effect of final drying temperature on rehydration of the granules.....	120
6.4.4. Remarks.....	120
6.4.4.1. Diffusivity.....	120
6.4.4.2. Influence of the water content on texture of rehydrated potato granules.	124
6.4.4.3. Practical limitation of water content in the product.....	125
CONCLUSIONS.....	126
REFERENCES.....	131
APPENDIX.....	140

LIST OF TABLES

TABLE		PAGE
1.	Relative humidity and vapor pressure of saturated salt solutions at 23°C	70
2	New F-T potato granules and pore size distribution: Important parameters and the maximums found in pore distribution and their related physical constants...	74
3	New add-back potato granules and pore size distribution: Important parameters and the maximums found in pore distribution and their related physical constants.....	78
4	The rehydration of potato granules stored for different periods of time at room temperature.....	97
5	Influence of storage time of the granules at room temperature on moisture content and rate of rehydration of F-T granules.....	99
6	Average initial moisture of different granules related to their rate of rehydration.....	103
7	Moisture sorption isotherms: Data for adsorption of new potato granules by F-T technique. Temperature: 23°C.....	104
8	Transient state data used in sample problem. Moisture adsorption of F-T potato granules with initial moisture content 3.59%.....	109
9	Influence of storage conditions on water content of the granules during the storage period.....	112
10	Final temperature of drying and corresponding moisture content and rate of rehydration of F-T potato granules.....	121

LIST OF FIGURES

FIGURE		PAGE
1	SEM photomicrograph (1000X) of pure starch granules...	34
2	SEM photomicrograph (1000X) showing an example of the vitreous structure of the granules of pure starch after gelatinization.....	34
3	SEM photomicrograph (200X) showing the aggregation of potato cells.....	36
4	SEM photomicrograph (500X) of the potato cell.....	36
5	A formation of cemented granules (200X).....	38
6	Partial conversion of the external surface into an internal surface.....	39
7	SEM photomicrograph (500X) of single potato granules forming an internal surface.....	40
8	SEM photomicrograph (200X); the formation of fissures.....	41
9	Porous and spongy structure (500X) of freshly produced granules by the F-T technique.....	43
10	A closer view (2000X) of the same granules (see Fig. 9).....	45
11	SEM photomicrograph (2000X) of the granules which were stored for a shorter time under certain storage conditions.....	45
12	SEM photomicrograph (500X) of old granules revealing the presence of grooves.....	47
13	SEM photomicrograph (2000X) of old granules revealing the presence of grooves.....	47
14	SEM photomicrograph (500X) of the cracks on the surface of the granules caused by cooling (-39°C).....	48
15	A closer view (2000X) of the same granules (see Fig. 14).....	48
16	SEM photomicrograph (1000X) of freeze-dried reconstituted fresh potato granules.....	50

LIST OF FIGURES CONTINUED

FIGURE		PAGE
17	SEM photomicrograph (1000X) of freeze-dried reconstituted old potato granules.....	50
18	SEM photomicrograph (1000X) of the filamentous structure of the old granules processed by the add-back process.....	51
19	Granular structure (5000X) of potato granules by SEM.....	51
20	SEM photomicrograph (100X) of potato granules processed by the add-back process.....	54
21	SEM photomicrograph (100X) of potato granules processed using the F-T technique.....	54
22	A meniscus of radius r, in a cylindrical capillary of radius r, with angle of contact ϕ.....	64
23	A cylindrical capillary of radius r_p, showing the "inner cylinder" of radius r_c.....	64
24	Adsorption and desorption isotherms of new F-T potato granules at temperature t = 23°C.....	73
25	Pore size distribution for the F-T potato granules....	75
26	Adsorption and desorption isotherms of new add-back potato granules at temperature t = 23°C.....	76
27	Pore size distribution for the add-back potato granules.....	77
28	Theoretical and experimental sorption curves for the surface condition $-D\frac{\partial C}{\partial r} = \alpha(C_s - C_o)$. Numbers on theoretical curves are values of $L = r\alpha/D$.....	90
29	The relationship between the total amount of diffusing substance (water) entering the granule and square root of the time.....	91
30	Sorption curves obtained using formula (6.4.2) in order to calculate diffusion coefficents (see Table 7 and Fig. 34).....	93
31	Effect of ageing on the rate of rehydration of F-T potato granules.....	98

LIST OF FIGURES CONTINUED

FIGURE		PAGE
32	The potential hydrogen bonding sites of the anhydroglucose unit of starch.....	101
33	Rate of rehydration of different potato granules.....	102
34	The rehydration rate of F-T potato granules stored at different relative humidities.....	105
35	The initial rates of rehydration taken from the curves of Fig. 34 versus water activity a_w.....	107
36	Effect of the controlled storage (a_w = 0) on the rate of rehydration of F-T potato granules.....	111
37	Effect of the controlled storage (a_w = 0.329) on the rate of rehydration of F-T potato granules.....	114
38	Effect of the controlled storage (a_w = 0.518) on the rate of rehydration of F-T potato granules.....	115
39	Thermal curves of old and new F-T potato granules and pregelatinized potato starch.....	117
40	The relationship between rates of rehydration of the F-T granules and the final moisture content (as shown in Table 10).....	122

INTRODUCTION

The potato, *Solanum tuberosum* L., is one of the largest food crops produced in the world today (Talburt, 1967). Because of high amount of starch, the potato is calorically important as a component of a human diet. It is also a very important dietary source of ascorbic and dehydroascorbic acids (Schwimmer and Burr, 1967; Smith, 1967).

Recent proximate analysis (Jadhav *et al.*, 1975) of the cultivar Netted Gem raw potatoes (avg. sp. gravity 1.098; 25% total solids) grown in southern Alberta gave a moisture content of 75.5%, protein 2.1%, raw fat 0.1%, carbohydrates 19.4%, crude fiber 0.5% and ash 1.1%. The analysis also showed the presence of 17.5% starch having 21.2% amylose.

The rapid expansion of the potato processing industry in the United States since 1946 is one of the significant developments in the food field during this period. Marked improvement in the quality of the existing products and the rapid development and successful introduction of a wide variety of new frozen and dehydrated potato products such as frozen french fries, dehydrated diced potatoes, potato flakes and potato granules, have made this expansion possible.

Recent statistics (Nicoll, 1970) show that Canada produced almost 19 million pounds of dehydrated potatoes. Cost of these products became moderate, particularly for the instant dehydrated mashed potatoes where the nature of the process used for manufacture, and the high bulk density resulted in minimum costs of packaging and of shipping (Boyle, 1967).

The instant dehydrated mashed potato includes potato granules and potato flakes. Potato granules are dehydrated, pre-cooked potatoes in granular form that can be quickly reconstituted to mashed potatoes by mixing with hot or boiling water (Feustel *et al.*, 1964).

Processing of potato granules with the aid of freeze-thaw (F-T) technique (in further text called the F-T process) (Ooraikul, 1973), although still in batch pilot size operation, has been chosen in this study since it has several advantages and all pros to become accepted in the industry. In comparison to the add-back process (Boyle, 1967) the advantages of this process over the add-back process are obvious. It requires simpler and smaller equipment to produce the same amount of product as it does not require the recycling of 85-90% of the dry product. The process is simple to operate and control. The quality of the product by F-T process is improved over that of the add-back process by the fact that:

a. it requires no recycling, hence no repeated heat treatment to damage the chemical and nutritional qualities of the product,

b. in the add-back process one poor batch of raw potato will affect the quality of a large amount of produce due to the recycling of the dry product,

c. the industry has been experiencing a variation of the reconstitution ratio of the granules to boiling water with the add-back product. The ratio has to be frequently adjusted. In the case with the F-T granules, there has never been such a problem. The ratio is consistently high at 4:1 (water:granules) for making reconstituted

mashed potatoes, whereas the add-back product can vary to a low ratio of 3:1; thus it makes it more economical to use the F-T product.

Furthermore, the reconstituted mashed potatoes from F-T potato granules repeatedly show superior textural quality to the add-back product and both the flavor and the color of the product are very close to those of freshly mashed potatoes (Ooraikul, 1974).

As far as the economical feasibility is concerned the only additional cost in F-T process is that of freezing (estimated 5% of the total processing costs of the granules). However, due to smaller equipment and simpler process the total capital investment in this process will be much smaller. The heating cost is estimated to be 10-20% less in this process.

As a result of the increasing market demand for extruded french fries in the last couple of years, a great deal of the dehydrated potato granules is used in the making of french fry mix. However, the potato granule industry has been experiencing difficulties in producing granules with a low water rehydration rate. So far, no explanation has been offered as to why sometimes one obtains a product with satisfactory rehydration rate and on other occasions, the granules produced are unacceptable for french fry production. This critical factor, the rate of rehydration of potato granules in cold water, is very important in producing high quality extruded french fries. It is highly desirable that the rate of water reabsorption into the dry granules be sufficiently low to allow uniform rehydration and mixing of the granules with water. A non-uniform rehydration which leads to wet and dry spots in the french fry dough is detrimental to the shape and appearance of the

french fries when extruded and to the texture and taste of the french fries when fried.

CHAPTER I

REVIEW OF THE LITERATURE

1.1. Processing of Potato Granules

Among the dehydrated potato products developed since the early part of this century, dehydrated mashed potatoes are one of the most popular, and production is still increasing. Potato granules were first developed in England during World War II and then introduced in the United States for home use in 1947 (Feustel *et al.*, 1964). Early technological development of potato granules have been adequately reviewed by Olson and Harrington (1955), Feustel *et al.* (1964) and Gutterson (1971). "Freeze and Squeeze" method (Greene *et al.*, 1949), spray drying of potatoes (Rivoche, 1951a, 1951b) and solvent extraction (Heisler *et al.*, 1953) were among the patented techniques to produce potato granules. Rendle (1945), Willetts and Rendle (1948) and Rivoche (1950) described in their patents the "add-back" process which requires recycling of substantial amounts of the previously dried granules to mix with the freshly cooked potatoes. This would reduce their moisture content down to levels at which granulation could be successfully achieved. According to Boyle (1967), the add-back process is still the only process being used commercially. Recently Ooraikul (1973) patented the freeze-thaw (F-T) technique for potato granule production consisting of the following steps: peeling, cooking, mashing, freezing and thawing, predrying, granulation, drying, cooling and sifting. Both the add-back process and the F-T process are limited: only potatoes of high total solids, generally above 20%, can produce mealy and fluffy mashed potatoes.

Both processes pass through very critical steps, such as cooking, mashing and granulation (Ooraikul, 1973). The biggest disadvantage of the add-back process is the recycling of the previously dried products. Only 1/10 to 1/6 of the dry potatoes coming from the dryer is the final product; the remainder stays in the system (Gutterson, 1971). The consequence of this is a high proportion of damaged cells in the product and possible extended microbial contamination. This process is also not well understood in terms of the raw material and the changes induced in it by the different stages of processing. The development of the F-T process was based on the finding by Greene *et al.* (1948) that freezing the cooked potatoes caused a remarkable toughening of the cell wall and a formation of free moisture, about 50% of which can be easily expressed from the potatoes after thawing without damaging the cells. They also found that a slow rate of freezing had no detrimental effect on the cooked potato cells. Harrington *et al.* (1951) reported that slow freezing, or quick freezing followed by slow thawing of cooked potatoes caused a freezing-out of water from the solubilized starch, leaving a firm structure. Reeve (1967, 1969) reported that freezing and thawing of cooked potatoes reduced the swelling capacity of the gelled starch and influenced its textural properties.

During the cooking step in the processing of potato granules, starch granules become gelatinized and pectic substances solubilized (Leach, 1965). This is a processing step where the potato tissue is prepared for mashing and subsequent drying operations. Overcooking or undercooking must be avoided in order to preserve desirable textural characteristics (Severson *et al.*, 1955; Harrington *et al.*, 1959). Steam cooking is considered to be most satisfactory (Ooraikul, 1973),

although cooking in boiling water may be beneficial for some substances (Burton, 1945; Hughes and Swain, 1962). Willard (1967) was of the opinion that potatoes have always been cooked wrongly because the high solids portions in the outer layers of the tuber, which require least heat treatment, have been receiving the most heat, and the center portions, which require the most heat, receive the least. In order to prevent this potatoes are sliced in 1/2" x 1/2" strips before cooking. Recently Warren and Woodman (1974) reviewed all important aspects concerning cooking of potatoes.

Mashing essentially involves the application of compressive and shear forces to the cooked potatoes so that, in effect, the individual cells can be separated from one another. Here, two phenomena are of importance: the binding force between the cooked cells and the strength of the cell wall (Ooraikul, 1973). The former determines the extent to which the cooked potato cells are separated and the latter determines the extent of damage sustained by the separated cells. The variety, specific gravity, starch content, anatomical parts of the potatoes, condition of cooked potatoes and methods of mashing have been reported to be the factors playing an important role in determining the proper mashing (Reeve, 1954a; Schwimmer and Burr, 1967; Greene *et al.*, 1948; Olson and Harrington, 1955; Harrington *et al.*, 1959; Ooraikul, 1973).

During the freezing step of the processing, the ice crystals formed by the moderate freezing rate should be sufficiently large to create minute passages through the cell walls to facilitate rapid drying (Ooraikul, 1973). Reeve (1954b) reported that slow-frozen cooked potatoes have a slightly greater porosity when dried than the quick-frozen ones and that freezing and thawing alter the moisture-reabsorption

capacity of the starch gels, while the length of time the potatoes remain frozen does not seem to be critical in the effects of freezing and thawing (Lazar *et al.*, 1964).

Pre-drying and granulation is well covered by the literature (Rendle, 1945; Rivoche, 1950; Cooley *et al.*, 1954; Potter, 1954; Severson *et al.*, 1955; Olson and Harrington, 1955; Harrington *et al.*, 1959; Hendel *et al.*, 1961; Lazar *et al.*, 1964; Ooraikul, 1973). The main aim of pre-drying is to reduce moisture content of the cooked mashed potatoes from approximately 76-80% to about 35-45%, before the mash can be successfully granulated to a fine powder without excessive cell damage which could significantly lower the textural properties of reconstituted mashed potato. In the F-T process (Ooraikul, 1973) the drying conditions in pre-drying are set such that the drying rate is at maximum. This is accomplished by high drying air temperature and high air velocity while the potatoes are slowly stirred at about 20 rpm. The heat and mass transfer rates in the bed are sufficiently high so that the temperature of the potatoes is kept low, *i.e.* maximum around 45°C (Jadhav *et al.*, 1975).

Pre-drying is followed by granulation, where the drying rate is dropped sharply to minimum. This is necessary as granulation can be accomplished quickly and efficiently at this stage by applying high compressive and shear forces on predried mashed potato through increasing the stirrer speed from 20 rpm to 500 rpm (Ooraikul, 1973).

In most cases, the granulated potatoes are dried in the airlift dryer to about 12% moisture, and finally dried to about 6% moisture in the fluidized-bed dryer (Olson *et al.*, 1953; Cooley *et al.*, 1954; Olson and Harrington, 1955; Severson *et al.*, 1955; Harrington *et al.*,

1959). In the drying step (Ooraikul, 1973), the drying temperature is increased to about 93°C and the air velocity is increased from about 0.15 ms^{-1} to about 1.7 ms^{-1}. The temperature of the produce should never exceed 85°C (Jadhav *et al.*, 1975). The F-T process is capable of producing a high quality product (Ooraikul, 1973; Ooraikul and Hadziyev, 1974; Ooraikul *et al.*, 1974; Ooraikul, 1974; Jadhav *et al.*, 1975). The broken cell count is ≈2% (Ooraikul, 1973, 1974), which is low when compared to 3-6% obtained with the direct processing technique described by Lazar *et al.* (1964). The product bulk density is reasonably high with bulk densities as high as 850 kg m^{-3}. The process is also capable of producing a very high percentage of fine granules, *i.e.* -60 mesh. Recycling of the coarse particles poses no observable problem in this process.

A recent study by Jadhav *et al.* (1975) showed the advantage of the F-T over the add-back process as far as the retention of Vitamin C in the granules is concerned.

I.2. Effect of Processing on Potato Cell Separation

I.2.1. Potato cell structure

We have to distinguish the starch from the potato granules. Potato granules, the subject of the present study, are instant dehydrated mashed potatoes. They are dehydrated, pre-cooked potatoes in granular form and their composition besides the starch includes proteins, pectic substances and some other constituents such as carbohydrates, fats and minerals.

The product consists largely of separated, whole-tissue cells (Potter, 1954), which are further in the text also called single potato

granules. Before processing the cells are firmly connected to each other (Reeve, 1973). Each cell is surrounded with a cell wall. The average thickness of the cell wall varies from 0.52 to 1.05 μ depending on variety of potatoes and harvest maturity (Reeve, 1973). It was reported (Hoff and Castro, 1969) that potato parenchyma cell walls contain 28% cellulose, about 55 to 60% pectins and 7% hemicellulose. Amorphous pectic substances and hemicelluloses occur between cellulosic microfibrils (Esau, 1953). There are natural thin areas in walls of parenchyma cells, the primary pits (Esau, 1953). They are well distributed in parenchyma cell walls of potato tubers and vary from circular to oblong, or from about 1 to over 3 μ (Reeve, 1973), causing the walls to be weak structurally (Esau, 1953; Reeve, 1967; Reeve, 1973). The main component within the potato cell is starch in the form of starch granules which have the radial fibrilar structure. The radial sectors contract centrifugally and expand tangentially during heating, causing the lateral (tangential) bonds between radial fibrils to become weak (Sterling, 1974). Potato starch granules are larger and easier to gelatinize than those from most cereals (Potter, 1954).

1.2.2. Selection of potatoes for processing

High solids composition (or high specific gravity) is a criterion used in selection for dehydrated products (Talburt and Smith, 1959). High solids potatoes are mealy. They undergo ready cell separation upon cooking and are well suited for dehydrated mashed potatoes. They are also preferred for chips and french fries. Because such potatoes readily undergo cell separation upon cooking, they are not readily adaptable to manufacture of products requiring piece integrity such as in some canned or frozen soups, stews and salads (Reeve, 1967).

1.2.3. Cooking

Upon cooking of potatoes all the starch granules are rapidly gelatinized. As the process continues, some solubilized starch diffuses out of the cell through primary wall pits in the cellulose matrix (Reeve, 1954a). The tissue cells become distended by the swollen gel and tend to separate, particularly in mealy tubers, due to the degradation of pectic substances between and in the cell wall (Reeve, 1967; Reeve, 1973). The heat energy is thought to disrupt or weaken some of the bonds in protopectin molecules resulting in the increase in water-soluble fraction of the pectic substances (Bettelheim and Sterling, 1955). Most of the tissue cells of potatoes do not swell greatly upon normal cooking even though they may become well rounded after cooking to the point of ready cell separation (Reeve, 1967). The separation by cooking is even improved if potato tubers are kept in storage before processing; high amounts of insoluble pectic substances decrease with storage (Sharma *et al.*, 1959). Microscopic examination of cooked potato tissue showed that the large swollen starch granules completely filled the cells, and also that almost all of the cell walls remained intact after cooking (Ooraikul *et al.*, 1974).

1.2.4. Mashing

By mashing the cooked potato cells are separated (Boyle, 1967; Ooraikul, 1973) and examination of the potatoes mashed at temperatures close to that of cooking indicated that cell separation was easily accomplished with little damage to cell walls (Ooraikul *et al.*, 1974). During mashing, additives (surfactants) are added and they form clathrates (Birnbaum, 1963) with the amylose fraction that may have diffused out from the gel matrix of the broken cells, or through

the minute pits on the wall of intact cells. This formation of clathrates prevents the amylose from forming strong intercellular bonds, and hence the cells can be separated more easily in the mashing and granulation steps (Ooraikul, 1973; Ooraikul and Hadziyev, 1974). Physico-chemical changes, namely retrogradation, in the starch gel in cooked potatoes occur during further stages of the processing, through which the gel becomes less sticky and less soluble. Granulation is then easier to accomplish (Potter, 1954).

1.2.5. Freezing, thawing and granulation

Freezing and thawing of cooked potatoes reduces the swelling capacity of their gelled starch and influences the textural properties of frozen potato products (Reeve, 1967). The freeze-thaw step was a required one in the processing of potato granules, because this step made possible pre-drying of the mash at an elevated temperature in a stirred bed dryer, and granulation at room temperature or lower with only little damage to the potato cells (Ooraikul and Hadziyev, 1974). By freezing and thawing the resulting product is more granular and less gelatinous in texture (Rendle, 1945) and a remarkable toughening of the cell wall occurs (Greene *et al.*, 1948) which makes cell separation during granulation better accomplished (Ooraikul, 1973). Reeve (1967) also reported that in some instances freezing of a processed potato increases the tendency for cell separation.

All these facts give enough evidence that a great percentage of potato cells (single potato granules) will be separated from their mother tissue during the processing from the cooking to the granulation. If there is any original tissue left, it will be most likely separated during the process of sieving.

1.3. Potato Starch and its Characteristics Related to the Potato Granules

1.3.1. Generally on starch

Starch comprises some 65 to 80% of the dry weight of the potato tuber (Schwimmer and Burr, 1967). In the raw tuber, starch is present as microscopic granules in the leucoplasts lining the interior of the walls of the cells of the parenchyma tissue. The granules are ellipsoidal in shape, about 100 microns by 60 microns on the average. They are thus much larger than the average starch granules of cereal grains. The size distribution seems in general to be independent of the location within the tuber (Schwimmer and Burr, 1967). It is apparent that potato starch growth may proceed from the central line outward towards the starch periphery; the major contribution to starch growth could be due to intussusception (Hall and Sayre, 1970). The same authors also used electron microscopy in examination of potato starch granules and suggested that each starch granule is surrounded by a membrane.

The real amount of starch present in the potato tuber before processing depends upon the storage conditions (mainly time and temperature). In fact, it is a common practice in the processing industry to "recondition" the potatoes which have been previously stroed at 4.5°C or lower, at a temperature of around 18.5°C to reduce the amount of accumulated sugars and increase the amount of starch. This is closely related to the activity of the enzyme invertase and its inhibitor (Smith, 1967).

Starch consists of two main components; amylose, which is a polydisperse polymer of α-1,4-linked glucosyl residues with little branching, and amylopectin, which is a highly branched-chain glucose

polymer in which the side chains are attached through α-1,6 linkages (Schwimmer and Burr, 1967). Normal corn, rice, potato and sorghum starches contain 17-28% linear fraction (depending on starch species) and the balance are branched. Starches from wrinkled corn or peas are mostly made up of the amylose (70-75%). Waxy starches (corn, rice, sorghum) have no linear component - only the branched fraction amylopectin (Foster, 1965; Ziemba, 1965).

1.3.2. Water effect

In the natural state, starch exists in the form of discrete microscopic granules that are held together by an extended micellar network of associated molecules. As a result of this structural arrangement, starch is insoluble in cold water despite the fact that the starch molecule is highly hydroxylated and therefore hydrophilic. At room temperature, starch establishes an equilibrium with moisture in the surrounding atmosphere and absorbs water reversibly (Leach, 1965).

Normal starch granules swell to only a limited extent, approximately 35 percent in volume when placed in an atmosphere saturated with vapor (Hellman *et al.*, 1954). This limited swelling indicates that the starch granules are readily permeable to water. This is apparently a reversible effect because the starch may be dried again with no observable change in structure.

It is well known that the swelling power and solubility of starch granules vary widely depending on the source of the starch. High amylose corn starches, for example, are highly resistant to swelling and solubilization. Potato starch, on the other hand, due to low amylose content shows exceptionally high swelling ability. In

addition, the high swelling ability might also be ascribed to the esterified phosphate groups in the starch (Leach, 1965). Also, potato starch and wheat starch granules have similar rates of solubilization during gelatinization when compared to one variety of corn starch (amylomaize VII) and it appears that the ease of solubility is a function of amylose content within the starch granule (Hill and Dronzek, 1973).

Potato starch granules are larger and easier to gelatinize than those from most cereals. The granule sacks of gelatinized potato starch are easier to rupture than the swollen granules of cereal starches (Potter, 1954). Gel formation occurs through the formation of a three-dimensional network of starch molecules, particularly the long straight chain amylose molecules. These molecules become interlaced through attractive forces between the molecules and particularly through hydrogen bonding on water molecules.

1.3.3. Heat effect

When an aqueous suspension of starch granules is heated, the granules do not change in appearance until a sufficient energy level is reached to dissociate the relatively weak bonding in more amorphous areas between crystalline micelles. Then starch granules swell tangentially and progessively to form, eventually, a highly attenuated network of molecules held together by still persistent micelles. As a direct result of granule swelling, there is a parallel increase in starch solubility, paste clarity, and paste viscosity (Potter, 1954; Leach, 1965; Ziemba, 1965).

The breakdown of the structure of the starch granule upon heating in water is believed to begin in the more accessible and amorphous

intermicellar areas of the granule where the bonding is weakest. Evidently, the degree of association in these amorphous regions differs in individual granules of each starch species, and, consequently, the granules gelatinize over a temperature range rather than at a single temperature. Normally, the gelatinization temperature is not affected by the presence of the linear starch fraction (Kerr, 1950; Potter, 1954; Leach, 1965). The breakdown of the structure of the starch granule on heating in water takes place in three quite distinct phases:

a) During the first phase, water is slowly and reversibly taken up, and limiting swelling occurs. Viscosity of the suspension does not increase noticeably and the granule retains its characteristic appearance.

b) In the second phase, which starts within a small range of temperature at approximately 65°C, the granule suddenly swells, increasing many times in size, taking a great deal of moisture and rapidly losing its birefringence. The viscosity of the suspension rises rapidly. A small amount of starch becomes solubilized.

c) In the third phase, which takes place at increasing temperature, the granules become almost formless sacs. There is more soluble starch leached out. In cooling a rigid gel is formed (Kerr, 1950).

1.3.4. Retrogradation

Gelatinized starch undergoes physico-chemical changes, namely retrogradation (Olson and Harrington, 1955), which affects the texture and solubility of the product (Potter, 1954). Retrogradation is a

process whereby starch in the dissolved or hydrated state reverts to a water-insoluble form (Foster, 1965). It arises from the inherent tendency of starch molecules to bond with one another leading to an increase in crystallinity (Whistler and Johnson, 1948; Collison, 1968). Retrogradation has been thoroughly covered by French (1950), Potter (1954), Kerr (1950), Hellman *et al.* (1954) and Olson *et al.* (1953).

1.3.5. Effect of surfactants

Another important property of starch, particularly of the amylose fraction, is its ability to form "clathrates" with iodine and fatty acids (Birnbaum, 1963). The clathrates are formed with two distinct components: the host and the guest. The linear fraction of amylose acts as a host forming a helical configuration to enclose the guest molecules (Radley, 1968; Ooraikul and Hadziyev, 1974; Birnbaum, 1955, 1971). In the production of potato granules the formation of clathrates prevents the amylose from forming strong intercellular bonds. The addition of surfactants prevents the cause of the pastiness and their hydrophilic nature will increase the wettability of the granules enabling them to reabsorb water more uniformly.

1.3.6. Modification

Starch can be easily modified and this property of starch is extensively used in food processing industry. The modification involves a fundamental chemical alteration of the starch structure. Where processing conditions are likely to thin the starch paste, reducing its functional properties, the starch may be cross-bonded by chemical means to overcome this deficiency. Cross-bonding is simply the process of linking the chains of a starch together. The linkages are of all types; interlinear, linear-branched, inter-branched, and

even intra-branched. The granules of the cross-bonded starch are much less fragile and more resistant to breakdown by heat, acid and shear conditions (Ziemba, 1965; Ellinger, 1972; Chilton and Collison, 1974; Ghali *et al.*, 1973; Whistler, 1974; El Saadany *et al.*, 1974).

1.4. Starch and its Influence on Dough Formation

There is no literature information on the rehydration properties of potato granules and on dough formation for extruded french fries. However, there exists an industrial practice (Tamura, 1973), where the ratio water:potato granules for dough making for extruded french fries is known to be ~2:1. Some more information exists concerning the reconstitution of potato granules with hot water for making mashed potatoes (Ooraikul, 1973; Ooraikul, 1974). The textural quality of reconstituted dehydrated mashed potato products is the major characteristic that determines their acceptability. There have been many attempts to measure the overall textural quality of the products, the character of which is a complex combination of several attributes such as firmness, glueyness and smoothness. It is not possible for a single measurement to evaluate all these parameters. It was found (Ooraikul, 1974) that glueyness correlated most strongly with the overall textural quality of the samples.

A dough is a very complex system. It cannot be described in a simple way by a single coefficient of viscosity, nor by any other simple parameter (Hlynka, 1970). These indices change with time, with speed of mixing, and in general, with the previous total history of the dough. From the rheological point of view a dough could be considered as a fluid, plastic body and elastic material, and factors

influencing rheological porperties are water content, mixing and extrusion (Hlynka, 1970).

Water, starch, and, in some cases, proteins (*e.g.* gluten in bread-making), appear to be the major factors controlling the proper formation of the dough (Sandsted, 1961; Sair, 1967; Yasunaga *et al.*, 1968; Jongh, 1961; Hlynka, 1970; Sollars and Rubenthaler, 1971).

Potato starch undergoes very rapid and unrestricted swelling at relatively low temperature, indicating weak and uniform bonding. Yet at any particular level of swelling, potato starch gives less solubles than the cereal starches. Since the equilibrium moisture of potato starch is substantially higher than that of the cereal starches, it is conceivable that hydrogen bonding occurs through hydrate water bridges rather than by strong direct association of linear and branched molecules (Leach *et al.*, 1959).

The amount of water in a bread dough formula is limited; it appears that most of the water is bound. The fact that so little water is lost during baking (from 42to 37%) is an additional evidence of the small amount of free water in bread (Larsen, 1964). This is due to the hydrophilic substances to which water is firmly attached. With the ingredients like nonfat dry milk, soy flour, partially delactosed soluble milk albumin, etc., the percent of added water retained in the bread increases (Barber and Kennedy, 1958).

Adsorption of water by flour appears to be a bulk property of the material and not dependent on particle size. Water appears to be almost unique among liquids in its ability to form doughs from flour. There is evidence that water interacts with flour components through specific chemical groups, probably by a dipole-dipole type of

interaction (Bushuk and Winkler, 1957a). It was also reported (Bushuk and Winkler, 1957b) that the magnitude of the attractive force, *i.e.* the dipole moment of the sorbate molecule, apparently had no effect on the rate of adsorption. It seems, therefore, that the polar nature of the sorbate molecule is only a necessary condition for sorption on flour.

It is well known that the water-adsorptive nature of starch can be varied. This has been accomplished by disruption of the crystalline structure of starch by heat, by enzymes and by mechanical forces (Larsen, 1964). However, the hydration during bread dough formation is very much complicated by the fact that starch can adsorb water much more rapidly than can gluten, and gluten must be hydrated in order for a bread dough to form (Baker *et al.*, 1946; Sandsted, 1961; Larsen, 1964). Starch binds a portion of the water, occupies about 44% of the gas-free dough volume, and constitutes the solid portion of the dough. Hydrated gluten, though largely fluid in its action (Baker *et al.*, 1946) also has elastic properties from its cohesions and holds the fluid mass together (Baker *et al.*, 1946; Hlynka, 1970; Jongh, 1961).

In their work on the distribution of water in dough, Baker *et al.* (1946) found that in the dough of 73% absorption, 47.0% of its volume was aqueous solution, 44.2% hydrated starch, and 8.8% hydrated gluten. The hydrated gluten and the aqueous solution are closely associated and move together in the dough surrounding the starch and contributing fluid and elastic qualities to the dough while the starch adds puttylike properties to the dough. The ability of potato granules to form a dough differs from that of wheat flour. It appears that the kind of proteins present and their characteristics related to water are

responsible for the difference (Baker *et al.*, 1946). Because of the lack of gluten in potato granules, the dough made from the granules lacks the elasticity typical of wheat flour dough.

The starch alone seems to be responsible for dough characterics, *e.g.* dough prepared from starch alone behaves like a concentrated stable suspension, showing, among other properties, dilatancy (Jongh, 1961). The starch dough in general resembles the dough made from potato granules.

CHAPTER 2

OBJECTIVES OF THE INVESTIGATIONS

In this study, an attempt is made to explain the variability in the water rehydration rate observed in potato granules. Specifically, the study was concerned with the causes for a significant difference in the water rehydration rate of newly processed potato granules from different processing batches and between new granules and those which have been stored for a certain period of time (aged granules).

In a preliminary study, several approaches were considered due to the fact that potato granules contain a predominant percentage of starch (up to 80% on dry basis) which is a very specific compound in terms of water holding capacity and the ability to undergo retrogradation and modification, and therefore could control the rehydration characteristics of the granules.

The retrogradation of starch molecules takes place during the processing of potato granules. It is uncertain to what extent the retrogradation proceeds. This would not allow an effective control of molecular rearrangement which might take place in the final product.

The alteration of the starch structure can be easily done by modification. The literature reports many ways of modification but none of them deals directly with the effect of modification or rehydration properties of potato granules.

It is believed that the addition of surfactants also could influence the change of rehydration properties of the granules.

In this study the rate of rehydration of the granules was looked at

from the point of view of five physical variables which could contribute to the solution of the existing problem. These variables are:

1st variable: The outer surface of the granules.

The shrinkage and porosity of the granule's surface and the effect of these on the rehydration properties of the granules were studied. Also, it was observed whether the granules represent an agglomeration of potato cells or if they represent potato cells alone, and what effect the agglomeration could have on the surface structure of the granules.

2nd variable: The inner surface of the granules. Pore size and pore size distribution.

The sorption properties of the granules were studied. This would throw some light upon the internal structure of potato granules; it would determine whether or not potato cells (in dehydrated form) are porous, how large the pores are, and how are they distributed since the porosity is a factor which dictates the sorption characteristics of the granules. This would also show to what extent the pores influence the penetration of water into the granules.

3nd variable: Diffusivity.

The effect of the cell's structure on water permeability was studied to see whether the

penetration of water into the cells occurs mainly through the pores or through the solid phase.

4th variable: Water content.

The effect of a change of the initial water content of potato granules on their rate of rehydration during the reconstitution with water was studied.

5th variable: Molecular rearrangement.

The possibility of the existence of molecular rearrangement within the granules during the storage was presented.

CHAPTER 3

MATERIALS AND PREPARATIONS OF MATERIALS

3.1. Raw Potatoes

The potatoes used were the Netted Gem variety grown in Southern Alberta. The specific gravity was between 1.086 and 1.090, which corresponds to 21.2-22.1% total solids. The specific gravity of potatoes was determined by the technique developed at the Food Science Department, University of Alberta (Redshaw and Fong, 1972; Redshaw and Fong, 1973). Before processing, the potato tubers were stored at 4°C and reconditioned at 18°C for 15 days.

3.2. Preparation of Potato Starch from Raw Potato

Purified starch from raw potato was prepared to obtain a scanning electron microscopic picture of the starch granules. This was important for the comparison of sizes of the starch granules, potato cells and potato granules. The method described by Johnson *et al.* (1968) was slightly modified. 75 g of washed tuber was ground for 10 min in a Waring blendor with 300 ml of water and crushed ice, containing 1% of ammonium oxalate, 100 ppm of sodium bisulfite and 1 ml of octyl alcohol as antifoaming agent. The mixture was poured into a 100-mesh sieve and washed with a small amount of water. The residue was reground and sieved in the same way and then washed with a small volume of water. All liquid portions were combined and poured through a 200-mesh sieve and further purified by several centrifugations at 2000 rpm. The light

brown upper layer of protein was removed while the lower was resuspended in distilled water until no impurity was evident under the microscope. The purified starch was washed twice by decantation with each of 95% ethanol, ethyl ether and acetone and then air dried.

3.3. Potato Granules

3.3.1. Processing of potato granules with the aid of freeze-thaw technique

The following materials were used for the F-T processing carried out in the pilot plant, Department of Food Science, University of Alberta:

Sodium bisulphite (anhydrous).	Fisher Scientific Co., Fair Lawn, N.J.
Additives:	
Myvatex 3-50	Eastman Kodak Company.
Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT)	Nutritional Biochemicals Corporation, Cleveland, Ohio.
Tetrasodium pyrophosphate	Fisher Scientific Co., Fair Lawn, N.J.
Hobart vegetable peeler	The Hobart Mfg. Co. Ltd., Don Mills, Ontario.
Hobart vegetable slicer	The Hobart Mfg. Co. Ltd., Don Mills, Ontario.
KitchenAid Mixer	The Hobart Mfg. Co. Ltd., Troy, Ohio.
Atmospheric Steam Cooker	
Stainless steel trays	

Air blast freezer with minimum air temperature of -29°C and air velocity of 1.42 m^3/s.

Manesty Petrie Fluid Bed Dryer, Model MP.10.E.,	Manesty Machines Ltd., Speke, Liverpool, U.K. Modified by Ooraikul (1973).
Canadian Standard Sieve Series and Portable Sieve Shaker	The W.S. Tyler Company of Canada Ltd., St. Catharines, Ontario.

The processing method was described by Ooraikul (1973). Essentially it involves peeling, slicing, washing, cooking, mashing, freezing, thawing, pre-drying, granulation and drying.

3.3.2. Add-back process potato granules and french fry mix

The add-back process (Boyle, 1967) potato granules were obtained from Vauxhall Foods Ltd. (Vauxhall, Alberta). The french fry mix was obtained from Chipper Foods Ltd. (Weston, Ontario).

3.3.3. Bulk density determination of the granules

The bulk density of the product was measured by pouring the granules into a 250 ml graduated cylinder to the 200 ml mark while tapping the cylinder until no further packing of the granules occurred (Ooraikul, 1973). The 200 ml volume of the granules were then weighed and the bulk density was then calculated in kg/m^3.

3.3.4. Potato dough and freeze dried reconstituted potato granules

3.3.4.1. Preparation of the potato dough from potato granules

The dough was prepared by simulating conditions for the reconstitution of granules as used in industry for the manufacture of extruded french fries. Thirty grams of potato granules were fed slowly through a glass funnel into 62.4 ml tap water (temperature about 19°C)

in a 600 ml beaker which was being vigorously stirred with a magnetic stirrer. The dough was conditioned for 10 min at room temperature before use.

3.3.4.2. Preparation of the freeze dried reconstituted potato granules

Potato granules were reconstituted as described above. A thin layer of dough was spread on an aluminum pan of 12.2 cm diameter and was quickly frozen. The frozen sample was placed for 30 hr in a freeze dryer (The Virtis Company, Gardiner, New York, Model FFD-42-WS). The dried powder was used to prepare the specimen for making SEM-photomicrograph.

CHAPTER 4

OUTER SURFACE OF POTATO GRANULES

4.1. Introduction to Scanning Electron Microscopy (SEM)

The possibility to have the third dimension available using scanning electron microscopy (SEM) has opened the field for the study of fine structures of starch granules and has yielded encouraging results.

The literature on scanning electron microscopy (SEM) covers quite extensively the surface structure of starch granules, and the information obtained could be very useful in explaining the behavior of potato granules.

Aranyi and Hawrylewicz (1968) were among the first cereal chemists realizing the importance of SEM. Comparing this technique with light microscopy, transmission electron microscopy and X-ray diffraction and investigating structural characteristics of flours and doughs, they were able to notice at higher magnification the surface character of both samples with more details.

Evers (1969) studied the structure of starch granules from wheat endosperm using SEM. He found considerable variation in form among both large and small granules of the same sample. Confirmation of the presence of an equatorial groove in large granules and its absence from small granules provided evidence in support of the different modes of formation of these two types. According to Badenhuizen (1965) the granules grow by apposition and they are densest in the outermost layers,

which possibly reflects a weaker crystalline structure and reduction in thickness near the center of the granule as well as susceptibility to collapse.

Starch being a transparent crystal often gives images which are difficult to precisely define with the light microscope due to the diffraction and other effects, such as internal structure, which may appear as a surface phenomena (Evers and McDermott, 1970). SEM, however, gives only surface detail (Hall and Sayre, 1973). The added advantage over light microscopy is that the granule under study may be rotated so it can be viewed from all sides. Further, any tilt angles between 0° and 80° can be employed along with rotation thereby allowing a more detailed analysis of granule shapes and surface detail. As a result, it is possible to accurately differentiate between what is actual surface and what is internal detail in a starch granule.

Using SEM Pomeranz (1972) reported an extensive dissolution of the protein matrix as the result of partial breakdown of cell walls in the center of the starch endosperm of malted barley.

Headley *et al.* (1972) using SEM showed the appearance of differently treated starch granules from corn grits. Small pieces of material, presumably protein, could be seen adhering to the starch granules. The nature of the association between starch granules and adhering proteinaceous particles was not determined. Recently, Cumming and Tung (1975) using SEM showed that starch granules play an important role in formation of protein fibril structure in wheat flour doughs. Dronzek *et al.* (1972) reported the presence of the grooves on the surface of starch granules extracted from the kernel. They also observed the difference in the mode of enzymatic attack on the large A-type and the

smaller B-type granules suggesting that the physical structure of these granules is probably different. Additional differences were observed between A and B-type starch granules using SEM. Gallant *et al.* (1972) reported that, after the enzyme α-amylase from *Bacillus subtilis* has penetrated into the grain, the attack on the internal region is more rapid in potato than in wheat and corn starches. This is in accordance with the suggestion that in the crystalline regions of type-B granules the polymer molecules are more loosely bound than in those of type-A starch granules.

Miller *et al.* (1973) used SEM to explain the increase in viscosity of a heated wheat starch-water suspension. The increase in viscosity was due mainly to the exudate released from the starch granule, which after freeze-drying a fully heated starch suspension, could be seen as a filamentous network. It is well known that an exudate is released as untreated starch is heated in water. In addition to this, it is also known that gelatinization is a function of temperature only. What is not so well known is that this material is released in relatively large amounts as the temperature approaches 90°C. Not all of the exudate originates from within the granule. This was especially true of waxy maize and potato starch granules where it could be seen that the exudate originated from all parts of the granule which became itself a very open, filamentous structure after freeze-drying. The voids developed in the wheat starch granules were shown as the exudate left the granule. This is evidence that many of the granules have a structure that could be considered approximately 50% network.

Barlow *et al.* (1973) using SEM reported that the entire area between starch granules of wheat is filled with material staining as

protein. Water-soluble proteins are confined to a position immediately surrounding starch granules, and this area is capable of rapid swelling on hydration. These soluble proteins associated with granules form an electrophoretically complex group.

An outstanding SEM study concerning starch and its gelatinization was conducted by Hill and Dronzek (1973). They proved that this technique can be useful for studying the changes in granule structure during gelatinization in conjunction with other physical methods like light microscopy (swelling), plane polarized light microscopy (loss of birefringence) and chemical methods for determination of the amounts of solubilized starch and the amount of amylose in the solubilized starch. Swelling and deformation of the starch granules observed in the scanning electron microscope corresponded to the loss of birefringence observed in the light microscope. At increased temperature (60°C) changes in the granule structure become evident. Larger granules appear to be broken down initially leaving granule residues that appear to be adhesive and extensible.

4.2. Application of SEM to Potato Granules

4.2.1. Method

The samples of dry potato granules were mounted on small disk-shaped metal sample holders (stubs) with a silver print adhesive. The granules were poured onto the surface of the stubs, and the excess was removed with compressed air blown over the sample holder. The samples were coated with carbon and gold in the vacuum evaporator to prevent charging of the specimen in the electron beam. The carbon and gold layer was approximately 100 Å. The mounted specimens were examined

in a S4 Stereoscan scanning electron microscope (Cambridge Scientific Instruments Ltd., Cambridge, England) at an accelerating potential of 15 KV. The samples were viewed by scanning the total specimen, and a representative area was photographed on Plus X and polaroid films.

4.2.2. Introduction

It is obvious that a solid possesses larger surface area if it exists in the form of fine particles. In our experiments we have dealt with particles having an average diameter below 250 microns. These particles were obtained by using a 60 mesh Tyler screen scale sieve, which had a nominal wire diameter of 0.180 mm and a sieve opening of 0.250 mm. These measures corresponded to No. 60 sieve in the U.S. Sieve Series with standard sieve openings of 250 microns.

There is an inverse relationship between the specific surface (the surface area of 1 g solid) and its particle size. The specific surface is given by the expression $S = \frac{6}{\rho L}$

where ρ is the density of the solid and L, as for an idealized case such as cube particles, the edge length. In practice, fine particles (the primary particles) to a greater or lesser extent tend to stick together to form aggregates or secondary particles under the influence of surface forces (Gregg and Sing, 1967).

Figure 1 shows an SEM photomicrograph of pure starch granules obtained from fresh potato. The aggregation of starch granules is obvious. The picture also reveals a smooth surface, without cracks, fissures or pores. This smooth outer view may be due to an ultrathin membrane which covers the outer surfaces of the granules. In such a case, a hilum hole may be covered over and, hence, not be seen in these

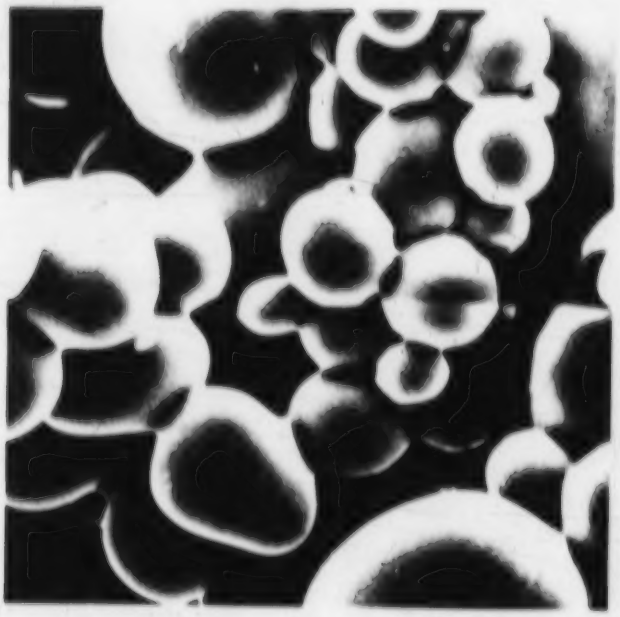


Fig. 1. SEM photomicrograph (1000 X) of pure starch granules

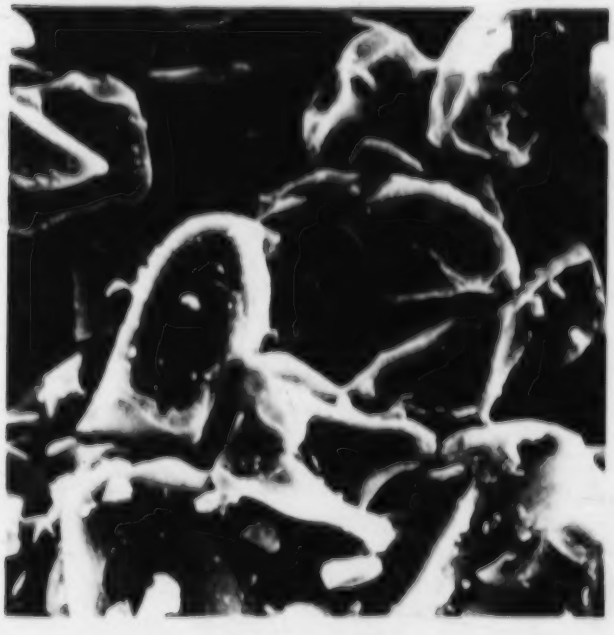


Fig. 2. SEM photomicrograph (1000 X) showing an example of the vitreous structure of the granules of pure starch after gelatinization.

micrographs. If an uncovered hole did exist at the surface of the granule, the scanning electron microscope would easily pick up such a detail. The presence of an ultrathin membrane might be due to the starch which grows on the granule surface by apposition although there is evidence that the intussusception may be a major method of starch growth (Hall and Sayre, 1970; van Lonkhuysen and Blankestijn, 1974). An SEM photomicrograph of gelatinized pure starch (Fig. 2) showed no such agglomeration but rather vitreous structure of the granules, after potato starch had been heated in the water at 65°C. The binding forces were weak and overwhelmed by the swelling forces (Leach, 1965).

4.2.3. The formation of aggregates. Pore volume.

There is evidence that potato cells can aggregate during the final drying period (Boyle, 1967). Shear forces involved and friction between granules during fluidization are contributing factors towards the acceleration of a spontaneous process of formation of aggregates (Gregg and Sing, 1967). However, the particles also may become "cemented" together through the action of adsorbed water during the storage period. In addition, the adsorbed water can promote the mobility of the ions derived from organic or inorganic salts present around the surface of the solid particles. Consequently this mobility could bring about an ionic interaction among the individual particles, which may result in additional agglomeration. Figure 3 shows a typical example of aggregation of potato cells. These aggregated particles become predominant in the later stage of the final drying. Figure 4 shows the SEM photomicrogram of a potato cell which forms part of an aggregate. This is rather an atypical example. The potato cell is round, nicely shaped ("polished"). This could be the result of the friction between the

Fig. 3. SEM photomicrograph (200 X) showing the aggregation of potato cells.

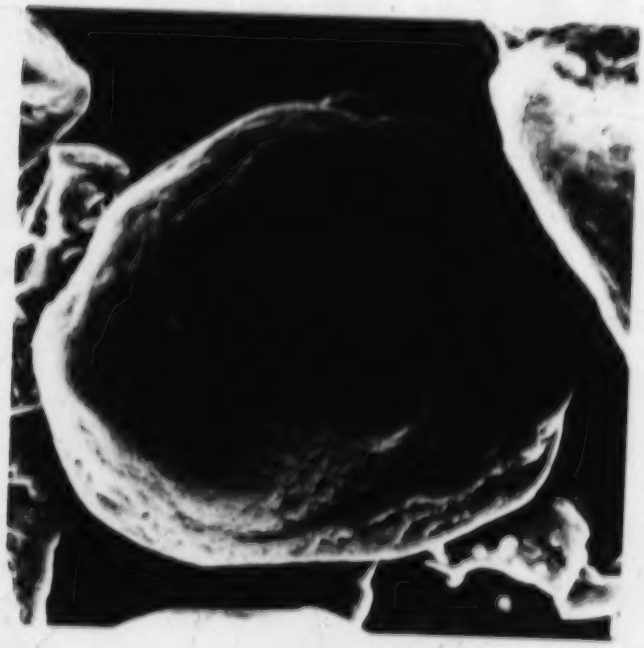


Fig. 4. SEM photomicrograph (500 X) of the potato cell.

cells or cells and granules during fluidisation. Most of potato cells or granules are otherwise angular-shaped and shrunken.

Figure 5 shows the aggregates of potato cells. This picture is taken at the end of final drying and represents a typical appearance of F-T potato granules as a final product. Comparing to Fig. 3 the granules are smaller due to the further shrinkage of the cell walls caused by drying, and shaping caused by shearing forces involved in drying. The upper right granule represents a granule rather than potato cell. The size and appearance speak in favor of this. The size is almost the same as the size of the granule in the middle of the picture and careful observation of the upper right granule shows the outlines of the cells which formed the granule. This gives the impression of a cemented granule.

Besides their specific surface, the aggregated single potato granules possess a pore volume made up of the gaps between the particles. This volume often amounts to a considerable fraction of the "lump volume". Many of the pores are thus comparable in size and related in shape to the primary particles themselves. A large specific surface may arise not only by the aggregation of primary particles, but also by the removal of parts of a parent solid in such a manner as to leave pores. The walls of these pores will comprise the "surface area" of the resultant solid (Gregg and Sing, 1967).

4.2.4. External and internal surface. Fissures.

In a discussion of surface properties of solids, it is necessary to distinguish between the external and the internal surfaces of the solid. The surface of any fragment derived from larger solids usually has cracks and fissures, some of which may penetrate into the

50 μ

Fig. 5. A formation of cemented granules (200 X)

fragment very deeply, and these will contribute toward the internal surface. The demarcation line between the external and internal surfaces has to be drawn in an arbitrary way, but despite this, the distinction between an external and internal surface is useful in practice: a wide range of porous solids have an internal surface greater by several orders of magnitude than the existing external surface, the total surface of solid thus being predominantly internal.

Figure 6 shows schematically the developing of a pore system, in which part of the external surface becomes converted to an internal surface.

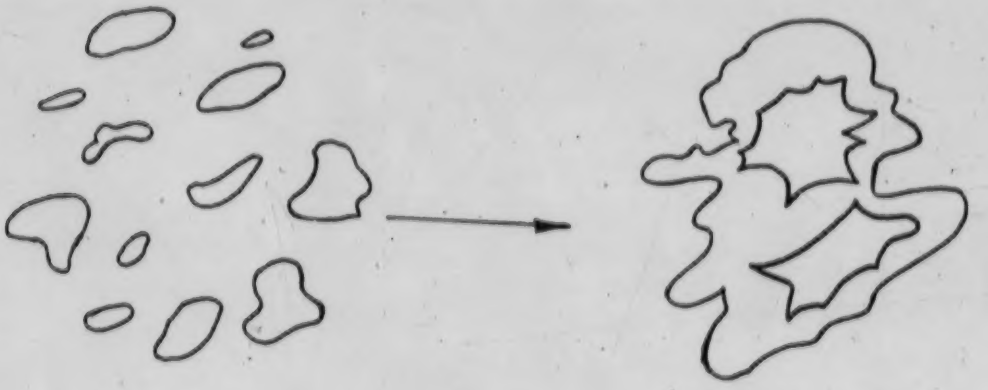


Figure 6. Partial conversion of the external surface into an internal surface.

Figure 7 is a typical illustration of the beginning of a formation of an internal surface as the result of the aggregation of single potato granules (cells). These forms of granules were obtained during an early stage of the final drying, although they could be found among the granules after the drying cycle has been completed. Figure 8, which

Fig. 7. SEM photomicrograph (500 X) of single potato granules forming an internal surface.

Fig. 8. SEM photomicrograph (200 X): the formation of fissures.

represents the formation of fissures, shows that fissures on the surface of such aggregates of granules may penetrate very deeply thus contributing towards an increase in an internal surface area. The forces binding the primary particles together within an aggregate, vary considerably in strength from one batch of potatoes to another. In extreme cases the forces may be so weak, that the particles may become pried apart, as for example, in the course of an adsorption experiment in which the swelling force can become the overwhelming force. Note the netted surface structure of the cells on the upper left part of the picture. This is supposed to be the cellulose part of the cell membrane.

During reconstitution of freeze-thaw granules with water, the surface area directly exposed to water plays an important role. The more single granules have been aggregated, the smaller the surface area of contact. This applies to those aggregations which are able to reveal the cemented structure. However, this is not the case with those aggregations still revealing the very porous structure or the presence of the fissures. When considered from another angle, freshly produced freeze-thaw granules stored and exposed to moisture might swell resulting also in the destruction of the aggregates due to the weak binding forces which keep the primary particles together.

4.2.5. Porous structure

Figure 9 shows the aggregation of the cells of freshly produced granules by F-T potato process revealing porous and spongy structure (magnification 500X). Note a shruhken part of the cell on the lower left part of the photomicrograph. The impression is that the inside of the cell is "empty", the result of part of the gelatinized starch being leached out. The lower right part of the photomicrograph

Fig. 9. Porous and spongy structure (500 X) of freshly produced granules by freeze-thaw technique.

shows a single angular-shaped granule (cell). There is an interesting finding by Banks *et al.* (1974) who reported that as the amylose content increased to 50% the number of angular-shaped starch granules decreased and more rounded forms became common (maize starch). Whether this could explain the presence of angular-shaped potato cells or granules in the final product, remains to be determined.

Figure 10 provides a closer view of the lower left granule from Fig. 9. The surface of the granule looks spongy and porous. The presence of pits on the surface contributes to this impression. These pits could be the points where water will penetrate easily into the granules during rehydration.

Figure 11 shows a part of the surface of the same granules, which were stored for a short time, up to six days, under controlled conditions (RH = 32.9%, t = 23°C). The surface of the granule does not appear as spongy as in the previous case when the granules were not stored. The less spongy structure could be the result of certain swelling induced by adsorbed moisture during storage. In a case when the forces among the granules are not so weak, the result of swelling may cause an expansion of a single potato granule. This expansion could close some of the existing fissures, which means smaller surface area of the granule--aggregation as a whole, and consequently possible slower rehydration rate during reconstitution.

Further examinations of the SEM pictures have shown the surroundings of the aggregations and single potato granules to be rather clear. There was no detectable presence of protein matrix as was found in some other studies (Aranyi and Hawrylewicz, 1968; Robutti *et al.*, 1974), neither was any kind of degradation observed in the form of an erosion (Dronzek

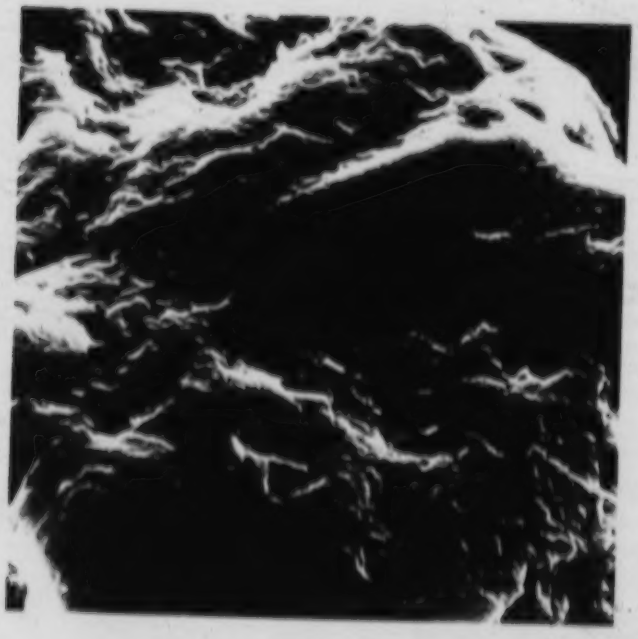


Fig. 10. A closer view (2000 X) of the same granules (see Fig. 9).

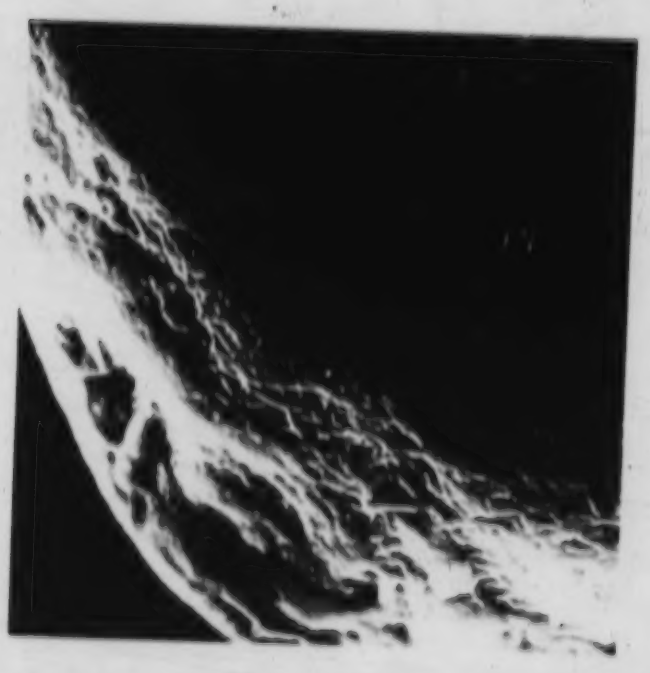


Fig. 11. SEM photomicrograph (2000 X) of the granules which were stored for a shorter time under certain storage conditions.

et al., 1972).

As illustrated by Figure 12 and Figure 13 (500X and 2000X magnification), the presence of grooves on the surface of old granules was sometimes observed. The last figure has also opened a very interesting, close view structure of potato granules.

In the preliminary study on rehydration properties of the granules, it was believed that the remaining bound water in the dried product (potato granules) could be frozen at low temperature (-40°C). This treatment is supposed to cause the starch molecules to realign and enable them to associate, the result of which is a decreased solubility of the starch molecules. The result of that was a very interesting network structure of the granules, when the granules were observed under the SEM. The SEM photomicrograph showed the cracks on the surface of the granules (see Fig. 14). Part of this photomicrograph was magnified 2000X (see Fig. 15). The structure of the granule within the crack is nicely visible. The network represents the dry cellulose part of cell membrane, while the edge is made of exudate of starch which has been gelatinized and lost its individuality.

In order to get evidence of a possible relationship between granules' pore structure and rate of rehydration, the granules were reconstituted and freeze-dried. The presence of a rigid ice structure at the location where sublimation occurs during freeze-drying mechanically prevents the shrinkage to occur to any great extent. The lack of shrinkage provides an internal porosity volume approaching the initial volume of water or ice within the granules. Sublimation of the water and presence of the solid constituents completely immobilized, leaves behind a light microporous structure of substantially the same dimensions as the original sample.

Fig. 12. SEM photomicrograph (500 X) of old granules revealing the presence of grooves.

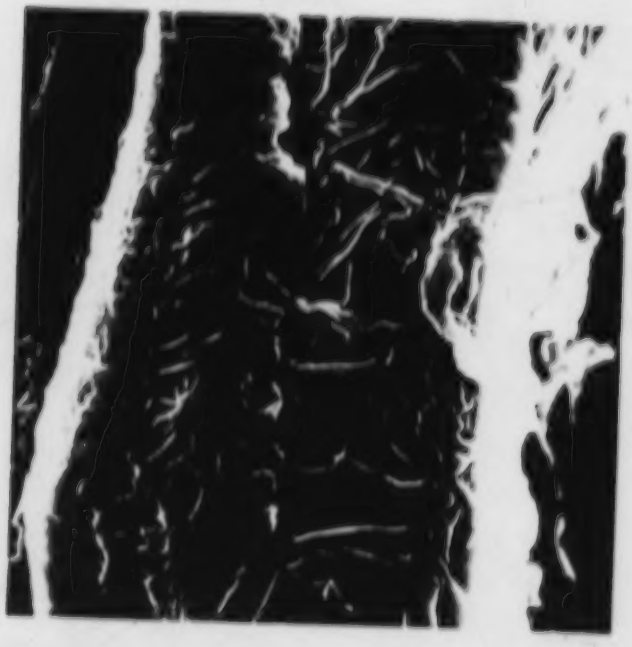


Fig. 13. SEM photomicrograph (2000 X) of old granules revealing the presence of grooves.

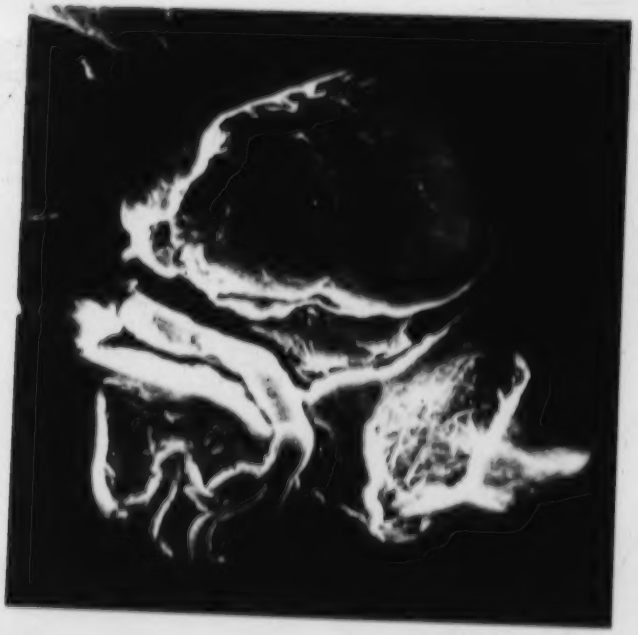


Fig. 14. SEM photomicrograph (500 X) of the cracks on the surface of the granules caused by cooling (-39°C).

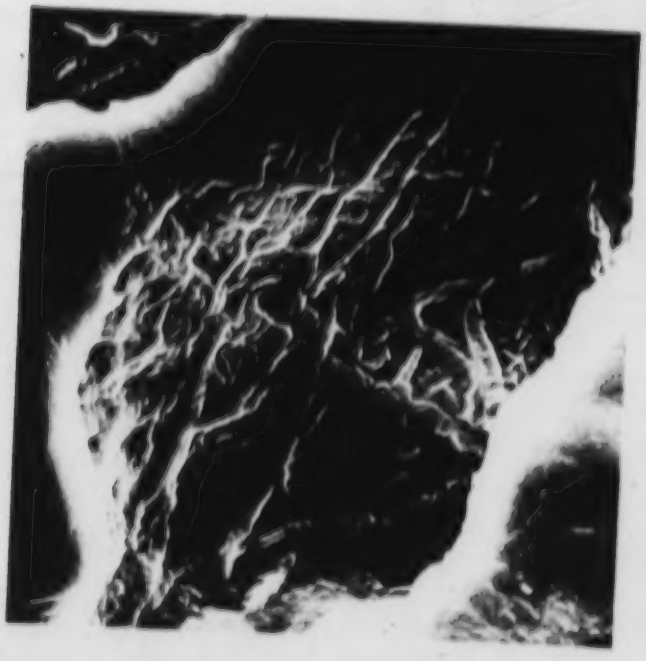


Fig. 15. A closer view (2000 X) of the same granules (see Fig. 14).

The process of sublimation and the resultant unchanged shape of the granules could reveal at least the sites from where water was removed. In other words, if it is assumed that during rehydration water penetrates into the interior of the granules to specific sites (voids), then these voids might be revealed by scanning electron microscopy. More voids on the surface of the granules might suggest that such granules rehydrate faster.

To clarify this photomicrographs were taken of freshly produced F-T potato granules and old granules from the same batch. The examination of these photomicrographs led to one important conclusion; there was no doubt any more, of the existence of two different surface structures, one for freshly produced freeze-thaw granules and one for old granules. The former showed very open, spongy surface structure, which could explain fast water absorption during rehydration (Fig. 16). Some filaments are visible, probably the result of the exudate originating from within the cells or could be the fragments of broken cells or filaments of cellulose. As stated by Miller *et al.* (1973), the exudate probably accounts for much more water absorption than the visual granules themselves. Contrary to this observation the same granules, but kept in storage for one year, showed rather close surface structure, which could explain the slow water absorption during rehydration (Fig. 17). The old granules processed by the add-back process showed almost the same appearance, except better revelation of the filamentous structure of the granules (Fig. 18). Some granules at magnification 5000X showed very interesting dense granular structure with each granule having a diameter of 0.5 μ or less (Fig. 19).

Additional information is needed to explain the nature of this

Fig. 16. SEM photomicrograph (1000 X) of freeze-dried reconstituted fresh potato granules.

Fig. 17. SEM photomicrograph (1000 X) of freeze-dried reconstituted old potato granules.

Fig. 18. SEM photomicrograph (1000 X) of the filamentous structure of the old granules processed by add-back process.

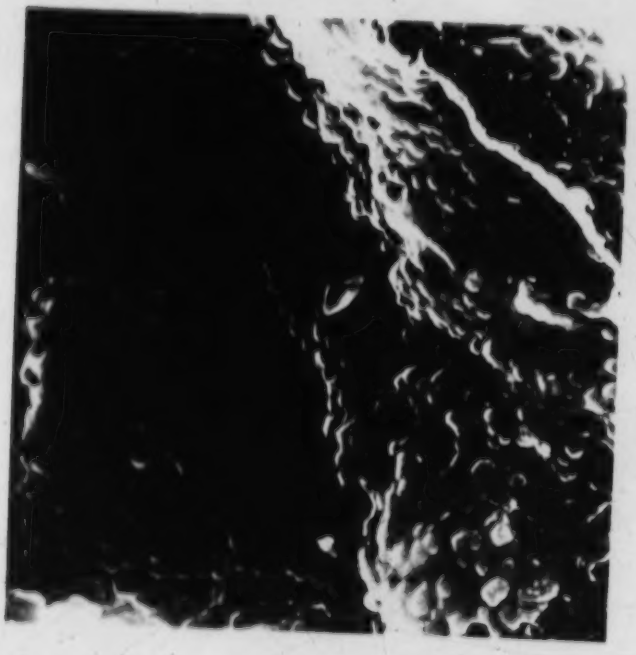


Fig. 19. Granular structure (5000 X) of potato granules by SEM.

granular structure, though the diameter of these granules, *i.e.* 0.5 μ or less, is very close to the molecular size of some natural polymers like starch. It was reported by Foster (1965) that molecular weight of amylose is in the range of 10,000 to 700,000 and of amylopectin in the range of 50,000 to 7,000,000 with the radius of gyration of 334-935Å for amylose and 820-2500Å for amylopectin. If we take, for example, the value of 2000Å as a radius of gyration, this corresponds to a diameter of 0.4 μ which is very close to the diameter of the granules, 0.5 μ or less, as observed in our study. Using Reeve's work (1967; Fig. 5), these granular regions could be also explained as small ungelled starch granules. Also, small granules could represent a deposit of precipitated material (probably amylose) that was dissolved from the gelatinized starch (Sterling, 1974; Fig. 10).

4.2.6. Size and shape of granules and bulk density

Dehydrated potato granules production was developed with the aim of producing a quality product with high bulk density to save packaging, storage and shipping costs. High bulk density is achieved by producing the finest possible granules. In the early development of the processing techniques it was not possible to subdivide the mashed potatoes into fine granules of essentially unicellular units. With the introduction of the add-back process and freeze-thaw technique, it became possible to produce much finer granules, generally smaller than 60 mesh size (Ooraikul, 1973). Cooley *et al.* (1954) found, however, that although the bulk density of smaller granules is higher, the rate of drying rather than the granular size is responsible for the important variations in bulk density. They found that the granules dried at slower rates have higher bulk density.

There is a difference in bulk density between potato granules processed by the freeze-thaw technique (Ooraikul, 1973) and potato granules processed by the add-back process (Boyle, 1967). Our measurements showed the following:

potato granules
(freeze-thaw process) . . . . . 740-760 kg/m^3

potato granules
(add-back process). . . . . 940-970 kg/m^3

One of the reasons that the add-back process granules consistently showed a higher bulk density is that the process of granulation followed after mash-mix has been cooled and conditioned for at least one hour. This markedly improved the granulation. Besides this, mash-mix (cooked potatoes have an average of 78% water and recycled granules around 12% water) has around 40% water content at which level the potato cells are most resistant to mechanical forces applied during granulation; the potato cells can be separated easily to fine powder without excessive cell damage. After granulation, the mix is dried down to 12% moisture and sieved. The rate of drying is slower than it is in the freeze-thaw process, and this could give higher bulk density of the product (Cooley *et al.*, 1954).

When SEM was applied to study these granules, the aim was to differentiate and partly to give the explanation for different bulk density obtained for the granules processed by the add-back process and for the granules processed using the freeze-thaw technique. As seen from Figure 20 and Figure 21, the cells and their aggregations obtained by the add-back process are smaller than those obtained by the F-T technique. The difference in the shape of the granules is also quite clearly visible. Add-back granules resemble round shape and F-T granules

Fig. 20. SEM photomicrograph (100 X) of potato granules processed by add-back process.

Fig. 21. SEM photomicrograph (100 X) of potato granules processed using the F-T technique.

are angular-shaped.

It is not unusual to have angular-shaped potato cells in the final product, since that is their original natural look. Reeve (1967) pointed out that potato cells remain angular and polyhedral, as in their original raw state when frozen par-fries were thawed and soaked in cold water or in cooked potatoes before the point of cells sloughing. Therefore, if it is supposed that potato cells remain mostly angular shaped like they are in their original raw state, then aggregation of angular cells could give the granules of similar characteristics (angular shape). The possibility of cells sloughing is prevented during mashing by addition of surfactants and by freezing and thawing.

If this hypothesis is supposed to be the right one, the round shape of the add-back granules remains to be explained. During the mashing step of the add-back process which is called mash-mixing, the granules previously dried to 12% moisture are recycled and mixed with cooked potatoes. It is supposed that as the angular cells separate from their original state, they stick to dried granules and round them off and remain like that through the cooling and conditioning steps to the granulation. The origin of round granular forms of the final product is not known. Whether these forms are obtained during the granulation or after some other step of the processing remains to be determined.

4.2.7. Remarks

1. The granules of pure potato starch obtained from raw material have a diameter in the range of 10-50 μ.
2. The average mean diameter of potato granules is supposed to be 200 μ (Reeve, 1967). An abundance of particles smaller

and larger than that was found in this study. The smaller ones are the potato cells (single potato granules). They are shrunken and angular-shaped granules with spongy and porous surfaces. The pores are considered to be the pits. The larger granules (diameter 200-300 μ) are the result of aggregation of single potato granules (cells). The aggregates can possess a very porous surface structure with many voids and grooves, characteristics of a high rehydration rate, and can possess a surface lacking the porous structure, *i.e.* a cemented structure (diameter around 160 μ). This structure can be the result of either swelling due to adsorption of moisture during storage or due to friction between the granules induced by fluidization. Such a surface can cause a low rehydration rate during the rehydration. These conclusions are relevant only for fresh and old granules processed by the F-T technique.

The overall average diameter of potato cells is 100 μ.

3. There was only a negligible difference in surface structures obtained for the granules processed by the add-back process and by the F-T technique. Only the former showed more filamentous structure (Fig. 18).
4. Pit size measurements at the surface of the granules showed that the diameter of the pits is in the range of 1.5 to 10 μ. Fissures are in the range of 2.5 to 7.5 μ and grooves in the range of 1.5 to 2.5 μ.
5. Water adsorption during storage could cause the external change of the porosity. This does not mean that the internal size of the pores would change. Water transport from the surface of the

granule toward the inside of the granule largely depends on the internal structure, which was assumed to be porous with an internal surface area as the result of the deep penetration of fissures. Water transport through the outside surface of the cell seems to be unrestricted due to the relatively large pits, but they are rather rare. However, this could depend on whether the granules are newly processed or stored under certain conditions causing moisture adsorption and thus narrowing the existing pits due to the possible swelling. On the other hand, water transport into the interior of the granules is expected to be rather free due to the large fissures.

In order to try to clarify this, a study of the sorption properties of the granules was necessary. This would give us the information on adsorption and desorption properties of the granules, pore size and pore size distribution.

CHAPTER 5

INNER SURFACE OF POTATO GRANULES. PORE SIZE AND PORE SIZE DISTRIBUTION

5.1. Sorption Characteristics and Related Physical Properties

5.1.1. Theory of Sorption

Kuprianoff (1958) suggests that water may exist as free water, chemically bound water, and adsorbed water. The adsorption is a consequence of the field force at the surface of the solid (the adsorbent), which attracts the molecules of the gas or vapor (the adsorbate).

The amount adsorbed per kg of solids depends on equilibrium pressure P, the temperature T, and also on the nature of the gas and of the solid:

$$X = f[(P/P_o)T,\text{gas},\text{solid}] \qquad (5.1)$$

where P_o is the saturation vapor pressure of the adsorbate at the temperature T (Gregg and Sing, 1967).

Equation (5.1) is an expression of the adsorption isotherm, *i.e.* the relationships between the amount adsorbed and the pressure, for a given gas adsorbed on a given solid at a fixed temperature.

The isotherms which result from physical adsorption may for convenience be grouped into five classes - the five types nowadays commonly referred to as the Brunauer, Emmett and Teller (BET) classification (Brunauer *et al.*, 1938). If the solid is non-porous, in many and probably in the majority of cases, the adsorbed layer becomes indefinitely thick when the saturated vapor pressur ($P/P_o = 1.0$) is reached. For this kind of solid there are two different types of isotherms to be considered,

Type II and Type III. If, however, the solid is porous so that it has an internal surface, then the thickness of the adsorbed layer on the walls of the pores is necessarily limited by the width of the pores. Type IV and Type V isotherms correspond to this kind of solid (Gregg and Sing, 1967; Bimbenet *et al.*, 1969).

The isotherm can, in general, be divided into several regions depending on the state of the water present:

a) a region of monomolecular layer

b) a region of multimolecular layers

c) a region of capillary condensation.

No definite relative humidity can be stated for the crossover from one region into the next and they may overlap.

One important phenomenon that should not be avoided is the problem of hysteresis which occurs during desorption. The desorption hysteresis loop usually ends at the monolayer, but in some cases it extends down to a water activity of zero.

Several theories have been proposed to explain hysteresis. The theories are all based on the effect of water condensing in the capillaries.

From a technological point of view, if isotherms are to be used in predicting the drying time of food materials, it is the desorption branch of the isotherm which is of importance, and also in most cases thermodynamic equilibrium is more nearly complete on this branch of the isotherm (Labuza, 1968; Gregg and Sing, 1967; van Arsdel, 1963).

It is important to notice that a hygroscopic material will attain a definite moisture content if it is maintained in contact with air of constant temperature and humidity until equilibrium is reached, but the

moisture content of the different constituents may differ widely at equilibrium. It is of importance to note that the equilibrium condition obtained is not an equal moisture content in all materials, but an equal activity.

5.1.2. The BET theory. Equation and model assumptions

From a theory suggested by Brunauer *et al.* (1938) a relationship between relative humidity and amount of adsorbate has been determined and has been frequently referred to as the BET equation:

$$\frac{P}{X(P_o - P)} = \frac{1}{X_m C} + \frac{(C - 1)}{X_m C} \cdot \frac{P}{P_o} \qquad (5.2)$$

in which : X = kg of water per 100 kg dry solids at water-vapor pressure P

P_o = vapor pressure of pure water at the same temperature

C = a constant related to the heat of adsorption

X_m = kg of water equivalent to a monomolecular layer absorbed on 100 kg of dry solids

The basic assumptions made in the BET theory are:

a) The heat of adsorption for the first layer, is constant and equal to the heat of vaporization plus a constant heat due to site interaction;

b) The heat of adsorption in all layers above the first is equal to the latent heat of condensation;

c) The evaporation-condensation constants in all layers above the first are identical;

d) When P becomes equal to the saturation vapor pressure the adsorbate vapor condenses as an ordinary liquid on the adsorbed film, so that the number of molecular layers

becomes infinite on the surface, which is postulated to be freely exposed to the vapor phase; and

e) Adsorption occurs only on specific sites.

5.1.3. Practical use and limitations

The equation (5.2) can be simplified dividing the numerator and the denominator of the left side of the equation by P_o and assuming that $R = P/P_o = ERH/100$, to

$$\frac{R}{X(100 - R)} = I + SR \qquad (5.3)$$

in order to express vapor pressure as percent relative humidity and to simplify the calculation (Salwin, 1963; Strolle and Cording, Jr., 1965; Labuza, 1968; Labuza *et al.*, 1970). Plotting the adsorption data in the form of $R/X(100 - R)$ against R, the straight line can be obtained in the range of 5-35% relative humidity, since the BET equation is restricted in validity to relative pressures below 0.30 or often less. From this plot a monolayer capacity can be calculated. In equation (5.3):

$$I = \text{y-axis intercept } \frac{1}{X_m C}$$

$$S = \text{slope } (C - 1)/100\ X_m C$$

If C is taken as $C = \frac{1}{X_m I}$ and substituted into the equation $C = (C - 1)/100\ X_m S$, one obtains:

$$X_m = \frac{1}{I + 100\ S} \qquad (5.4)$$

where X_m is the monolayer capacity expressed in kg liquid adsorbed per 100 kg dry solid.

It has been noted that a parallelism exists between adsorbability and condensability. This suggests that the forces involved in physical

adsorption are the same as in condensation, *i.e.* van der Waal's forces (Charm, 1971). The confirmation of this is the value of C in the BET equation which represents a constant related to the heat of adsorption by

$$C = \frac{a_1 \nu_2}{a_2 \nu_1} e^{(E_1 - \lambda)/RT} \qquad (5.5)$$

where: E_1 = heat of adsorption of molecules in first layer

λ = latent heat of condensation of water

$a_1 a_2$ = condensation coefficients

$\nu_1 \nu_2$ = the frequency of oscillation of the adsorbed molecules in a direction normal to the surface

The ratio $\frac{a_1 \nu_2}{a_2 \nu_1}$ has been shown (Gregg and Sing, 1967) to be very close to 1. Consequently, equation (5.5) reduces to:

$$C \simeq e^{(E_1 - \lambda)/RT} \qquad (5.5.1)$$

from which:

$$E_1 - \lambda = RT \ln C \qquad (5.5.2)$$

where $(E_1 - \lambda)$ is net heat of adsorption (Gregg and Sing, 1967).

The value of X_m from equation (5.2) is proportional to the specific surface $S(m^2/kg)$ of the adsorbent and according to Gregg and Sing (1967)

$$S = \frac{X_m}{M} \cdot N \cdot A_m \times 10^{-20} \qquad (5.6)$$

where:

X_m is expressed in kg of adsorbate per kg of dry solid and

M = molecular weight of the adsorbate

N = Avogadro's Number (6.023×10^{23} molecules per mole)

A_m = cross-sectional area of the adsorbate, *i.e.* the area which an adsorbed molecule occupies on the surface of

the solid in a completed monolayer, expressed in $Å^2$ ($1Å = 10^{-10}m$).

It has been proposed by Emmet and Brunauer (1937) that A_m can be calculated from the density ρ of the adsorbate in the ordinary liquid form, and with the assumption that the arrangement of the molecules at the surface is just the same as it would be on a plane surface if placed within the bulk of the liquid, under these conditions:

$$A_m = 1.091\left(\frac{M}{\rho N}\right)^{2/3} \times 10^{16} \qquad (5.7)$$

5.2. Capillarity

5.2.1. The Kelvin equation, assumptions and concept of critical radius (R_c) and thickness of adsorbed layer (t)

The Kelvin equation for cylindrical pores is given by:

$$\ln \frac{P}{P_o} = -\frac{2V^1\sigma \cos \Phi}{r\ RT} \qquad (5.8)$$

where: P = vapor pressure of a liquid contained in a cylindrical capillary (Pa)

P_o = saturation vapor pressure (Pa)

V^1 = molar volume of the liquid (for water $\frac{18\ kg}{\gamma H_2O}$)

σ = surface tension ($kg\ s^{-2}$)

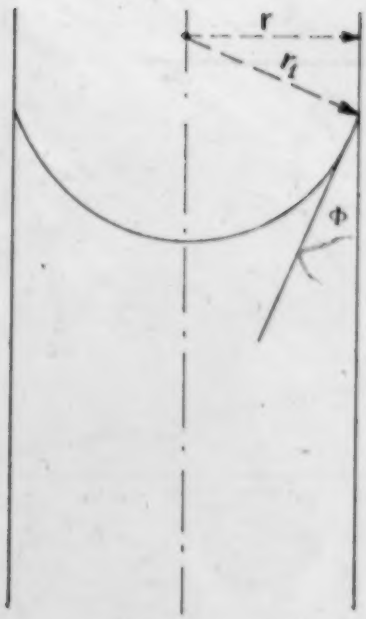
Φ = angle of contact between the liquid and the walls of the capillary

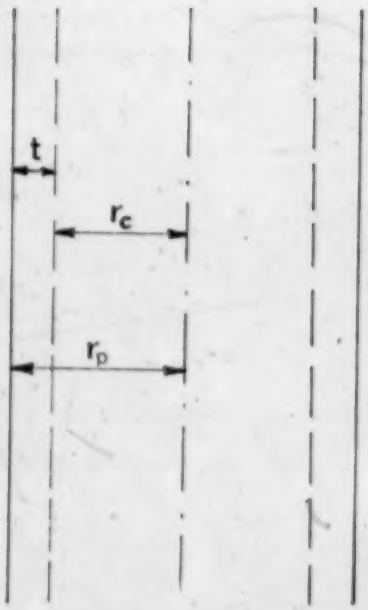
R = gas constant ($kgm^2s^{-2}kgmole^{-1}{}^0K^{-1}$)

T = absolute temperature (^0K)

r = cylindrical radius (m)

(Orr and Dallavalle, 1959), and making the simplifying assumption that $\Phi = 0$, *i.e.* that the liquid wets the walls of the pores, and defining





(from Gregg and Sing, 1967)

$r = r_l \cos\Phi$

if $\Phi = 0$, $\cos 0 = 1$;

$r = r_l$

Figure 22. A meniscus of radius r_l, in a cylindrical capillary of radius r, with angle of contact Φ.

Figure 23. A cylindrical capillary of radius r_p, showing the "inner cylinder" of radius r_c.

$r = R_p = R_c + t$ (see Fig. 22 and Fig. 23).

If this value of r is substituted in the Kelvin equation the critical radius R_c can be calculated

$$\ln\left(\frac{P}{P_o}\right) = -\frac{2V^l\sigma}{(R_c + t)\ RT}$$

$$R_c = \frac{2V^l\sigma}{RT\ \ln\left(\frac{P}{P_o}\right)} - t \qquad (5.8.1)$$

R_c is the critical radius of pores in Å ($\times 10^{-10}$m), above which all pores are still filled with adsorbed or condensed vapor. Knowing R_c

and t, the true radius (pore radius) R_p can be calculated from the relationship

$$R_p = R_c + t \qquad (5.8.2)$$

t is the thickness of an adsorbed film in Å ($\times 10^{-10}$m), assuming that the adsorbate completely wets the solid material and that at any point on the desorption isotherm, all pores are covered with an adsorbed film. As it has already been mentioned the calculation of t is restricted to the validity of the BET equation. The most direct way of estimating t is to measure the adsorption isotherm on a non-porous reference substance, having a surface as nearly as possible identical in nature with the porous solid which is considered, and to assume that at the same pressure the thickness of the multilayer thus evaluated is the same as on the walls of the porous solid. The monolayer capacity X_m of the reference solid can be estimated by the standard BET procedure and the adsorption X on this solid at any pressure can then be converted into the thickness of the film, by use of the relationship:

$$t = \frac{X}{X_m} \cdot \sigma_o \qquad (5.9)$$

or

$$t = n\sigma_o \qquad (5.9.1)$$

where σ_o is the average thickness of a single layer of adsorbed molecules and n is the number of molecular layers adsorbed. The value of σ_o is not necessarily the same as the molecular diameter d of the molecules, the relationship between σ and d depending on the mode of stretching of successive molecular layers in the adsorbed film. The calculation of t is restricted to the range of high pressures. The formula used in this study for calculation of t is:

$$t = \sigma_o \left[\frac{5}{2.303 \log Po/P}\right]^{1/3} \qquad (5.9.2)$$

(Gregg and Sing, 1967)

Negative sign in equation (5.8) implies that P will be less than P_o if the contact angle is less than 90°, a condition that is fulfilled by most, though not all, solid-liquid pairs. If a solid containing cylindrical pores of radius r is exposed to a vapor, the pressure of which is gradually increased, the vapor should condense as a liquid in the pores as soon as its pressure P reaches the value given by equation (5.8); conversely, if the pores already contain liquid, evaporation should not commence until the pressure of the vapor in the system falls to P, a value lower than the saturated vapor pressure and given by equation (5.8). If the capillaries are not all of the same radius, and the solid is exposed to a vapor with a fixed pressure P, then condensation to a liquid should occur in those pores having a radius equal to, or less than, the value r calculated from the Kelvin equation (Gregg and Sing, 1967).

5.2.2. Different types of pores

Generally, it is considered that solids possess porous and non-porous structure, each one having a different character of the physical adsorption.

If the solid is porous so that it has an internal surface (see Chapter 4) then the thickness of the adsorbed layer on the walls of the pores is necessarily limited by the width of the pores. The form of the isotherm is modified correspondingly; instead of a Type II isotherm we have a Type IV and instead of a Type III, a Type V (Gregg and Sing, 1967; Bimbenet *et al.*, 1969).

Most theoretical approaches to the problem of physical adsorption consider the pores to be either cylindrical or non-cylindrical, although there are five pore systems.

As far as the shape of the pores is concerned those having only one opening can have an "ink bottle" cavity and spheroidal cavities. It is also recognized that there are two shapes of the meniscus of condensed liquid being adsorbed within the capillaries: hemispherical, occurring along the desorption, and cylindrical, occurring along the adsorption and causing the pore to be open at both ends.

As far as the size of the pores is concerned, there are micro pores ($r < 10$ Å), macro pores ($r > 100$ Å) and transitional pores (10 Å $< r < 100$ Å).

5.2.3. Calculation of pore size distribution

In order to relate equation (5.8) to the amount adsorbed, a pore size distribution must be calculated.

From the Kelvin equation (5.8) the value of r ($r_1, r_2, \ldots$), corresponding to any given point on the isotherm, *i.e.* for any given value of the relative pressure $\frac{P}{P_o}$ ($\frac{P_1}{P_o}, \frac{P_2}{P_o}, \ldots$) and the value of adsorption X ($X_1, X_2, \ldots$), can be calculated. If the amount adsorbed on the walls is neglected, then X_1/ρ (where ρ is the density of the adsorbed vapor) would be equal to the volume $v_{r,1}$ of all the pores which have radii up to and including r_1. Hence, when the relative pressure P_1/P_o has been reached, all these pores will have become filled according to the capillary condensation hypothesis. If v_r is plotted versus r and by reading the slope of the curve at suitable small intervals of r, the pore size distribution curve could be obtained by plotting $\frac{dv_r}{dr}$ against r or $\Delta V_p/\Delta R_p$ against R_p, where ΔV_p are the decremental values of V_p and ΔR_p are suitable small decremental intervals of R_p. ΔV_p correspond to the area of the pore walls ΔS_p which is calculated from

$$\Delta S_p = 2 \frac{\Delta V_p}{R_p} \qquad (5.10)$$

where

$$\Delta V_p = \Delta V_k \left(\frac{\bar{R}_p}{\bar{R}_c} \right)^2 \qquad (5.10.1)$$

ΔV_k represent the decrement of capillary-condensed material and is obtained as the difference of the total decrement in the amount adsorbed (ΔV) and the amount desorbed from the film on the pore walls during the desorption step (ΔV_f)

$$\Delta V_k = \Delta V - \Delta V_f \qquad (5.10.2)$$

ΔV_f is calculated from the area of the walls covered with the film (*i.e.* the walls of the pores from which capillary evaporation has already occurred) and the diminution in thickness of the film during the desorption step, using the expression

$$\Delta V_f = 0.064 \times \Delta t \times \Sigma(\Delta S_p) \qquad (5.10.3)$$

where the values of $\Sigma(\Delta S_p)$ are obtained by the summation of all the preceeding lines for certain ΔS_p at certain P/P_o and represent the surface area of all pores not filled by capillary condensation.
S from equation (5.6) is used to calculate the average pore radius of the particles if all the surface is attributed to the walls of the pores and by assuming that all the pores are cylinders:

$$R_p = \frac{2V_p}{S} \times 10^{-10} \qquad (5.10.4)$$

where R_p = average pore radius in Å

V_p = pore volume in m^3 per kg of adsorbent

S = surface area in m^2 per kg of adsorbent (Orr and Dallavalle, 1959).

When just the pore volume of a porous adsorbent is required, it is necessary only to determine the volume of gas (vapor) adsorbed at the saturation pressure. At this point, unless the pores are quite large, the entire pore volume is filled with adsorbed vapor. If the amount of

vapor adsorbed on the external surface is small compared to the total amount adsorbed, which is frequently the case, the pore volume (V_p) is essentially equal to the volume of vapor in the adsorbed phase. If the mass of liquid adsorbed per kg of adsorbent at saturation pressure is m, then the volume of the adsorbed phase in the pore volume, V_p, per kg of adsorbent is:

$$V_p = \frac{m}{\rho a} \qquad (5.11)$$

where: ρa = density of the adsorbed phase.

Before capillary condensation occurs in a given pore there will already be an adsorbed layer on the walls; and conversely, when evaporation of already capillary-condensed liquid takes place, an adsorbed layer will be left behind on the walls. The thickness of this layer must be taken into account in calculations of pore size distribution by means of the Kelvin equation.

5.3. Application to Potato Granules

5.3.1. Methods

5.3.1.1. Water activity

In order to determine the ideal storage conditions for freeze-thaw and add-back process potato granules, the equilibrium moisture data were obtained by exposing previously dried granules (-60 mesh) to atmospheres of different relative humidities until the corresponding equilibrium moisture contents were reached. The required relative humidities were obtained using desiccators with standard saturated solutions of various salts (Table 1). The desiccators were stored at constant temperature (23°C). For most of the samples, equilibrium was reached in 6 days.

Table 1: Relative Humidity and Vapor Pressure of Saturated Salt Solutions at 23°C[1]

Salt Solution	% Relative Humidity	Vapor Pressure mmHg
Potassium chromate	86.5	17.98
Sodium chloride	75.5	15.69
Calcium nitrate	51.8	10.77
Magnesium chloride	32.9	6.83
Lithium chloride	11.1	2.31
Phosphorus pentoxide	0	0

[1]From Wink and Sears (1950)

5.3.1.2. Moisture content

The moisture content of the potato granules was determined by drying the samples until constant weight was reached (approximately 24 hrs) in a vacuum oven (90°C and 27 in Hg)

5.3.1.3. Sorption isotherms. Monolayer capacity. Heat of Adsorption

The new F-T potato granules previously dried were exposed to atmospheres of different relative humidities until equilibrium was reached. Plotting the gain in weight of the samples, expressed in kg water per 100 kg dry solids, versus water activity a_w (a_w = E.R.H./100 = P/P_o), the adsorption isotherms were obtained. To obtain desorption isotherms, the samples equilibrated on ERH = 100% were transferred to the atmospheres of lower relative humidities and kept there until equilibrium was reached. The loss in weight of the sample, expressed

again as kg water per 100 kg dry solids was plotted versus water activity a_w. Using adsorption data and equations (5.2), (5.3) and (5.4), the monolayer capacity (X_m) for new F-T potato granules was calculated.

Knowing X_m and using the expression $I = \frac{1}{X_m C}$ (p. 61), it was possible to calculate a constant C and knowing C and the latent heat of condensation of water (= 2446 kJ/Kg at the temperature t= 23°C) it was possible to calculate the heat of adsorption E_1 using equation (5.5.1).

The surface area corresponding to the monolayer capacity was calculated using equation (5.6).

5.3.1.4. Pore size distribution (PDT)

To obtain a pore size distribution, the desorption isotherms of F-T potato granules were used. Plotting $\Delta V_p/\Delta R_p$ against R_p a pore size distribution for the F-T potato granules was obtained.

ΔV_p was calculated from equation (5.10.1) and ΔR_p was a corresponding variation of R_p. R_p was calculated from equation (5.8.2) and the parameters R_c and t from equation (5.8.2) were calculated from equations (5.8.1) and (5.9.2). ΔS_p (from Table 2) was calculated using equation (5.10). Table 2 and Table 3 show the maximums found in pore distribution and their related physical constants as well as the important calculated values concerning the potato granules (see also the Appendix).

V represents the volume of liquid in m^3 adsorbed per 100 kg dry solids (adsorbent) or the volume of liquid in m^3 removed from solids calculated on 100 kg dry solids basis at certain P/P_o and which is determined directly from the experimental isotherms.

The system of claculations described above has been transformed

in a corresponding computer program (LeMaguer, 1974).

5.3.2. Results and discussion of results

From Figure 24, it appears that the adsorption isotherm is of the Type IV and this type is related to the porous material (Bimbenet *et al.*, 1969).

In Fig. 24 the upper intersection of ADS (adsorption) and DES (desorption) curves for new F-T granules (ADS = DES) was 32.9 kg water per 100 kg dry solids at P/P_o = 1.000, and lower intersection 3.71 kg water/100 kg dry solids at P/P_o = 0.050.

The optimum monolayer capacity for new F-T potato granules is X_m = 5.42 kg water per 100 kg d.s. Using this value, the specific surface of adsorbent (potato granules), which corresponds to the monolayer capacity, was obtained (S_{BET} = 268.20 x 10^3 m^2 per 100 kg d.s.) (Table 2). Heat of adsorption of molecules of water in the first layer was calculated and is E_1 = 6320 kJ/kg. The pore size distribution analysis (Fig. 25) showed that the F-T granules have two maximums with an average R_p = 15.4 Å and R_p = 6.1 Å at those maximums. The range of small pores with an average R_p = 6.1 Å appears to be larger (total area under the distribution curve A_{PDT} = 68.36%) than of big pores with an average R_p = 15.4 Å (total area under the distribution curve A_{PDT} = 31.44%) (Table 2 and Fig. 25).

For the comparison the sorption isotherms and pore size distribution analysis of new add-back potato granules were obtained (Fig. 26 and Fig. 27). The optimum monolayer capacity and the specific surface of the granules, which corresponds to the monolayer capacity, were not significantly different (Table 3). The add-back granules have greater experimental pore volume (V) and pore volume at Max PDT (V_p)

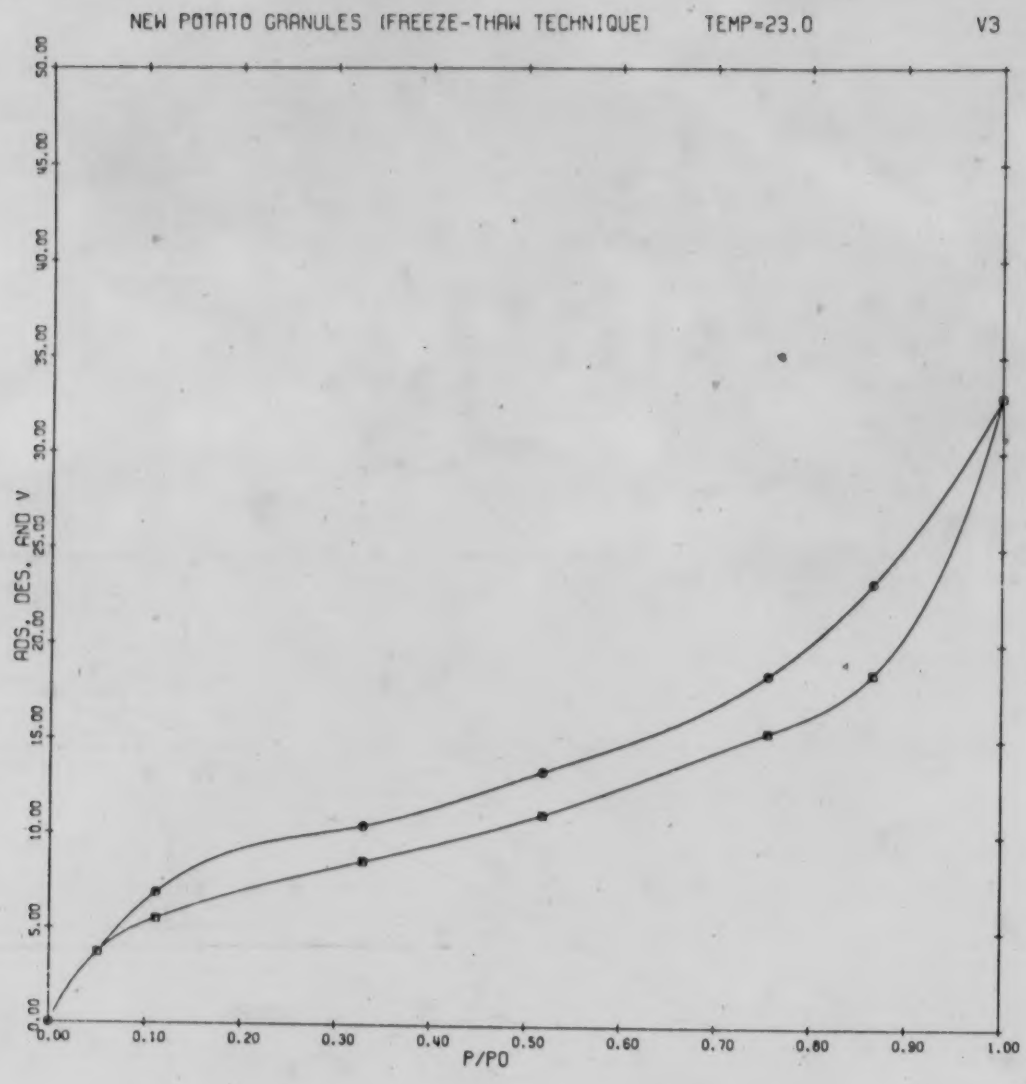


Fig. 24. Adsorption and desorption isotherms of new F-T potato granules at temperature t = 23°C.

Table 2: New F-T Potato Granules and Pore Size Distribution: Important Parameters and the Maximums Found in Pore Distribution and their Related Physical Constants*

P/P_o	V $m^3/100$ kg d.s. at STP	R_c Å	t Å	R_p Å	A_{PDT} Under the Curve area of PDT in %	$\Sigma\Delta S_p$ M /kg
0.410	11.5×10^{-3}	11.8	3.6	15.4	31.44	101.7×10^3
0.055	4.0×10^{-3}	3.6	2.4	6.1	68.36	411.0×10^3
				Total	100.00	

Heat of adsorption of molecules of water in the first layer, $E_1 = 6320$ kJ/kg

Optimum monolayer capacity $X_m = 5.42$ kg water/100 kg d.s.

Surface area corresponding to the monolayer capacity $S_{BET} = 268.20 \times 10^3$ m^2/kg d.s.

Pore volume at Max PDT (4.425) $V_p = 36.71 \times 10^{-3}$ m^3/100 kg d.s.

Pore volume experimental $V = 32.9 \times 10^{-3}$ m^3/100 kg d.s.

*Refer to pp. 67-69 where the meaning of the symbols is explained.

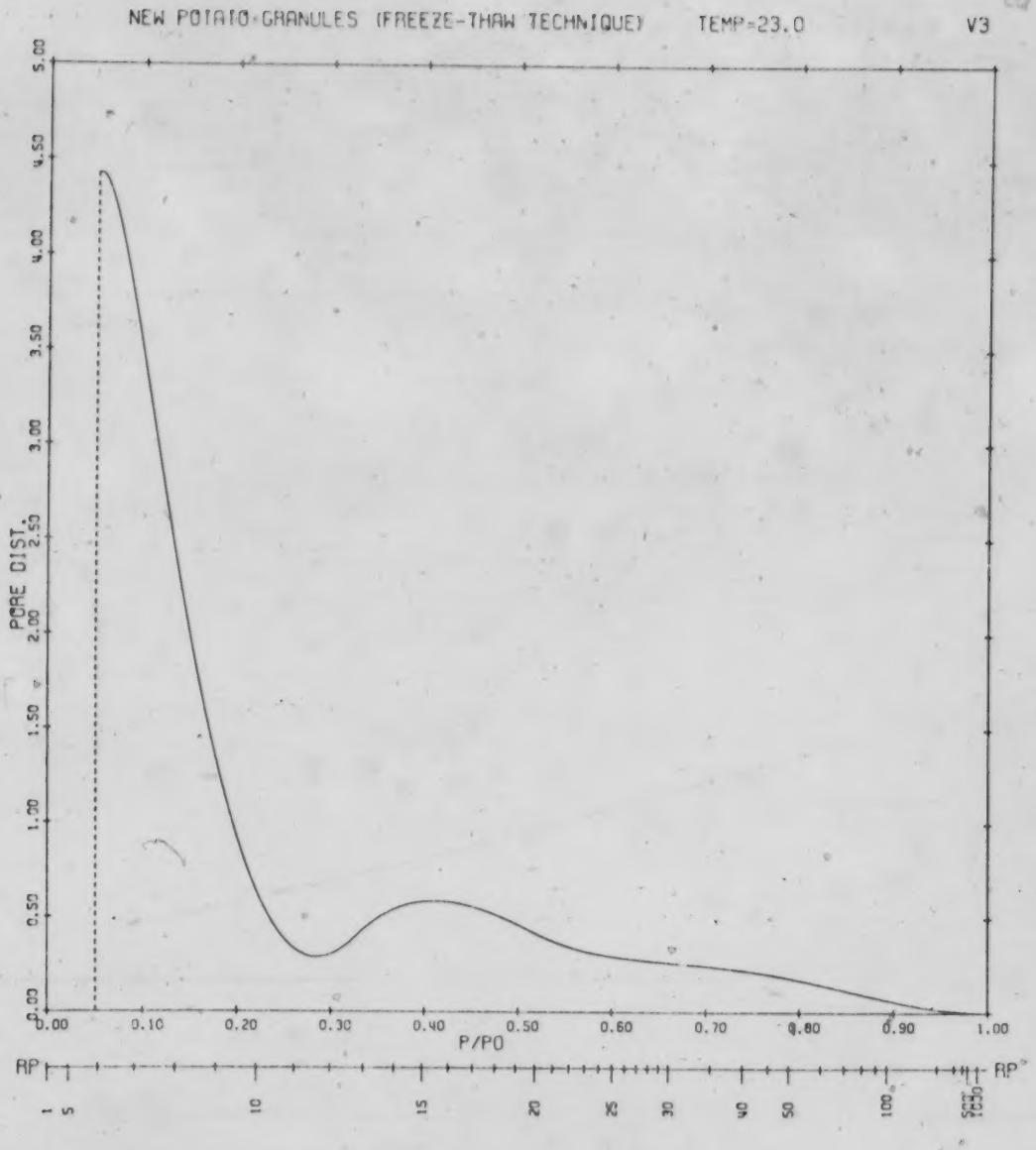


Fig. 25. Pore size distribution for F-T potato granules.

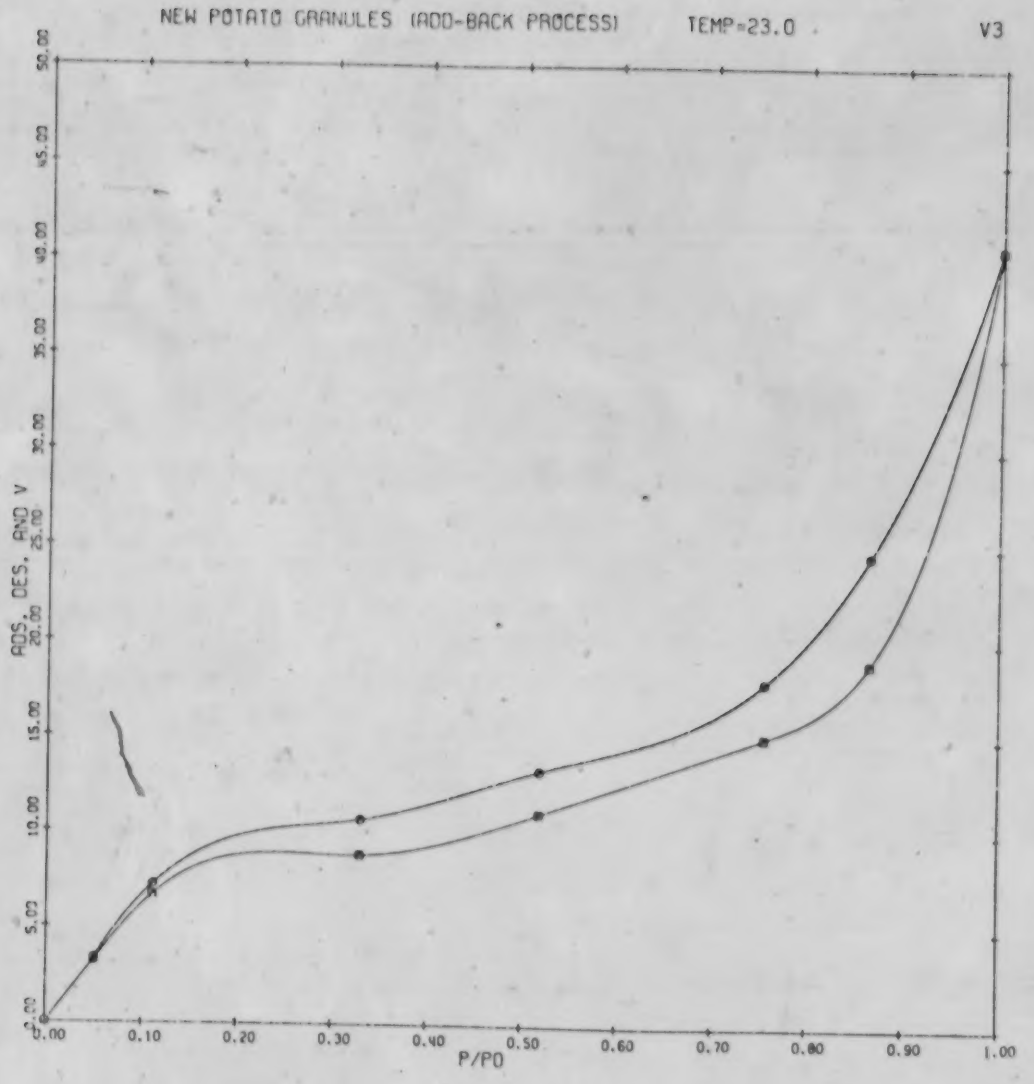


Fig. 26. Adsorption and desorption isotherms of new add-back potato granules at temperature t = 23°C.

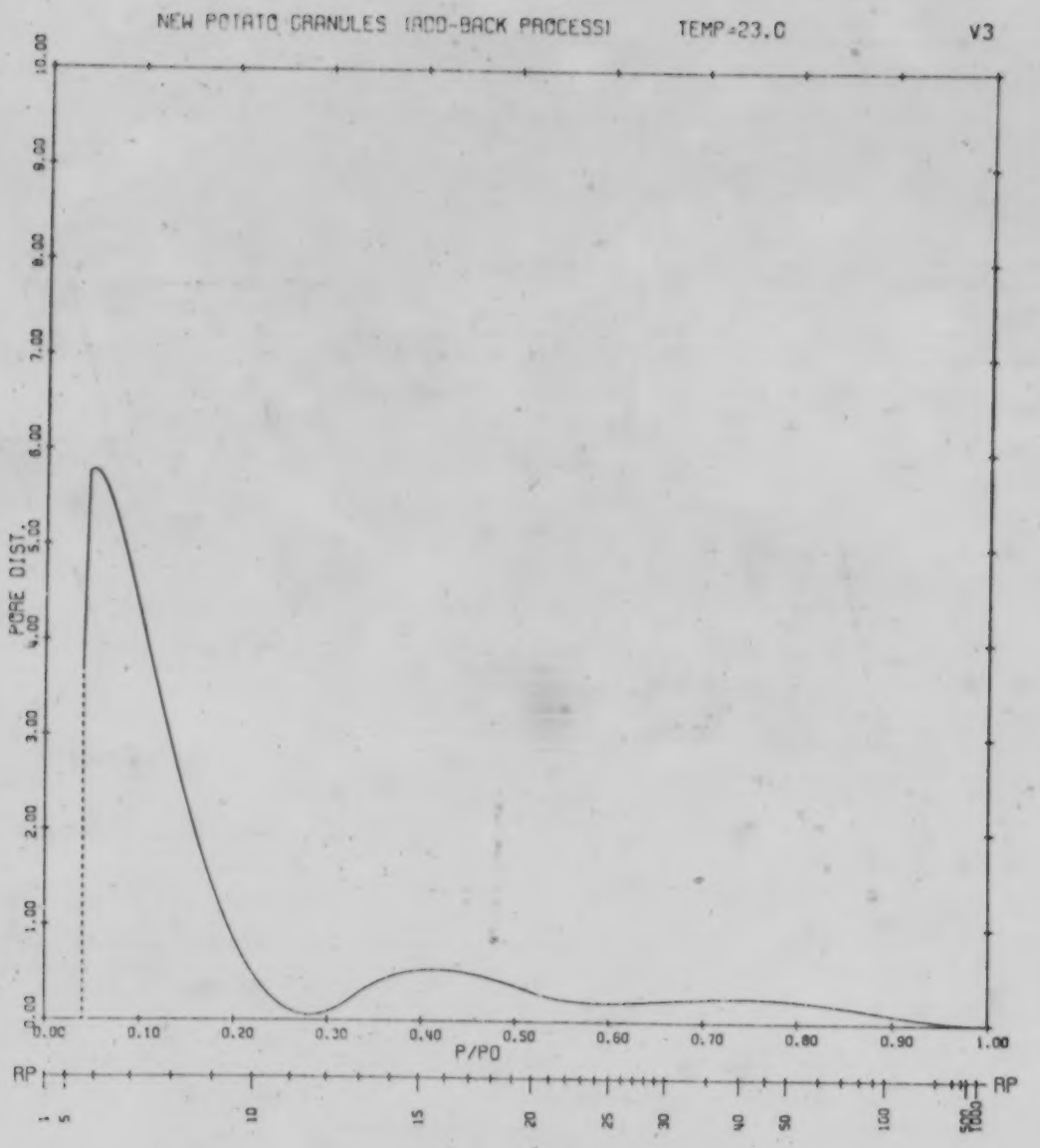


Fig. 27. Pore size distribution for the add-back potato granules.

Table 3: New Add-back Potato Granules and Pore Size Distribution: Important Parameters and the Maximums Found in Pore Distribution and their Related Physical Constants

P/P_o	V $m^3/100$ kg d.s. at STP	R_c Å	t Å	R_p Å	A_{PDT} Under the curve area of PDT in %	$\Sigma\Delta S_p$ m^2/kg
0.740	17.4×10^{-3}	35.0	5.2	40.2	9.47	50.0×10^3
0.415	11.7×10^{-3}	12.0	3.6	15.6	13.99	105.5×10^3
0.050	3.3×10^{-3}	3.5	2.4	5.9	76.54	486.4×10^3
				Total	100.00	

Heat of adsorption of molecules of water in the first layer	E_1 = 5684 kJ/kg
Optimum monolayer capacity	X_m = 5.55 kg water/100 kg d.s.
Surface area corresponding to the monolayer capacity	$S_{BET} = 275.01 \times 10^3$ m^2/kg d.s.
Pore volume at Max PDT (5.782)	$V_p = 46.20 \times 10^{-3}$ $m^3/100$ kg d.s.
Pore volume experimental	$V = 40.65 \times 10^{-3}$ $m^3/100$ kg d.s.

(Table 2 and Table 3). The pore size distribution analysis showed that the add-back potato granules have larger pore distribution having three maximums and larger range of small pores (A_{PDT}) (Table 3). Also, the add-back granules have small percentage of big pores (R_p = 40.2 Å, A_{PDT} = 9.47%) (Table 3). Taking this into consideration one can conclude that F-T potato granules are less porous than add-back potato granules which does not necessarily mean that F-T granules rehydrate slower when exposed to atmosphere of 100% relative humidity than add-back granules if they have the same initial moisture content.

The reason for that could be the presence of the skin around the entire surface of add-back granules (Berry, 1974), which is revealed when freshly rehydrated granules are examined under the microscope, or pore distribution itself. Namely, new F-T potato granules have larger pore distribution area with R_p = 15.4 Å at the maximum, than the summation of the distributions of add-back granules with R_p = 40.2 Å and R_p = 15.6 Å at the maximums, while new F-T potato granules have slightly smaller pore distribution area (= 68.36%) with R_p = 6.1 Å at the maximum, comparing to add-back potato granules.

5.3.3. Remarks

The optimum monolayer capacity of the potato granules corresponds very closely to the monolayer capacity of the potato flakes (5.1 to 5.8%; Strolle and Cording, 1965) which are dehydrated mashed potatoes in form of flakes obtained by drum-drying, and generally to all dehydrated potatoes (approximately 6%; Salwin, 1963). Surface area corresponding to the monolayer capacity is quite large ($\sim 270 \times 10^3$ m^2/kg d.s.).

The adsorption and desorption isotherms, which are of the Type IV, showed that potato granules are very porous (Bimbenet *et al.*, 1969).

This evidence is more valuable than the observations of the surface of the granules (SEM), since it gives the information of the internal structure of the granules.

Pore distribution analysis shows the predominance of small pores with an average pore radius $\overline{R}_p$ = 6.0 Å. This radius does not correspond to the radius of pits measured at the surface of the granules. The maximum radius of the pits was 50000 Å (=5μ) and minimum 7500 Å (≈ 0.75μ) and they are much larger than those found by the sorption experiment. Even the pores measured at the surface of the granules previously rehydrated and then freeze-dried (Fig. 19), showed the radius much larger (~0.3μ = 3000 Å) than the radius of the pores within the granules.

The pits, grooves and fissures which appear at the surface of the granules do not seem to be a part of the pore system which dictates sorption properties of the granules. However, they could contribute to the faster initial rehydration due to the large openings and surface area of the contact. The real resistance to the penetration of water through the granules seems to be due to the presence of the pores.

It is not only the pore size which could cause the resistance of the penetration of water into the interior of the granules and/or cells, but also the layer of adsorbed molecules of water. This layer covers the surface of the granules (cells) and the pores and resists the migration of coming water during rehydration.

Diffusion could be affected greatly as the result of that and it was decided to study some transport properties of the granules as they might be affected by initial water content of the granules.

CHAPTER 6

REHYDRATION STUDIES

6.1. Introduction

Newly processed F-T and add-back potato granules and the same ones but kept for a long time in storage show remarkable differences in their ability to adsorb the water. A preliminary study by Noraikul and Hadziyev (1973) was done to determine the cause of this phenomenon. Their suggestions were based on possibility of the retrogradation of starch molecules within the granules during storage.

Since the atmosphere of the storage was not controlled there was a possibility for water to have an effect on rehydration of the granules. This study was concerned with the influence of water on rehydration properties of the F-T potato granules.

The penetration of water into the granules during the reconstitution mainly depends on the ability of water to diffuse through the pores and/or solid phase of the granules. Therefore, it was first decided to study the diffusion process and the influence of water content of the granules on diffusivity.

6.2. Theory of Diffusion

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motions. Although the molecules do not have a preferred direction of motion, this is reconciled with the fact that the overall transfer takes place

from the region of higher to that of lower concentration (Crank, 1967).

The mathematical approach to the diffusion process is usually considered from the point of view of diffusion in an isotropic or an anisotropic medium. In an isotropic medium, the diffusion properties are independent of directions of the diffusing substance. In the anisotropic medium they vary.

Diffusion can occur in gases, liquids and solids. Diffusion in gases can be treated by application of the kinetic theory, but liquid and solid systems are less well understood and must be treated on a more empirical basis.

The geometry of the body is another factor which influences the study of the diffusion process; we have to distinguish between plane sheet, cylinder and sphere.

The diffusion coefficients are defined according to Fick's First Law, in which the "driving force" for diffusion is the concentration gradient

$$F = -D \frac{\partial C}{\partial x} \qquad (6.1)$$

Fick put diffusion on a quantitative basis by adopting Fourier's mathematical equation for heat conduction. From the above equation the rate of transfer (in isotropic substances) of diffusing substance per unit area of a cross-section is proportional to the concentration gradient measured perpendicularly to this section and the diffusion coefficient D. Diffusion coefficient can be taken as constant in dilute solutions, while at higher concentration and in high polymers it depends very markedly on concentration (Crank, 1967). The negative sign in equation arises because diffusion occurs in the direction opposite to that of increasing concentration.

Diffusivity is a physical property just as is thermal conductivity, and its value will be dependent on the temperature, pressure, and composition of the system. Thermal conductivity, however, is a property of a substance or material, whereas diffusivity is a property of a system.

If F from equation (6.1) is the amount of material diffusing, and C the concentration, and both expressed in terms of the same unit of quantity, *e.g.*, kilogrammes or kilogramme moles, then it is clear from the equation (6.1) that D is independent of this unit and has dimensions lenth^2 time^{-1} (m^2s^{-1}).

The fundamental differential equation of diffusion in an isotropic medium is derived from the above equation and is given in cartesian coordinates (obtained by the formulas for the transformation of spherical coordinates to cartesian coordinates) by

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) \qquad (6.2)$$

This equation assumes that D does not depend on the concentration of the diffusing substance. Equation (6.2) can be reduced for the case of an unidirectional transfer to

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (6.3)$$

i.e., if there is a gradient of concentration only along x-axis. Expression (6.3) is usually referred to as Fick's second law for diffusion.

D in equation (6.3) is the constant called the diffusion coefficient, or diffusivity.

6.3. Boundary Condition. Mass Transfer Resistance at the Surface

In this study we were interested in the diffusion of a liquid in a solid sphere. The initial and boundary conditions for this particular problem are uniform concentration C, at time 0 and constant concentration C_0 at the surface for all times. The solution is obtained using the method of Laplace transforms (Crank, 1967), which leads, for the total amount of diffusing substance entering or leaving the sphere, to the equation:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\Pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-Dn^2\Pi^2\theta/r^2} \qquad (6.4)$$

During its movement towards the center of the sphere, the diffusing substance can either enter the sphere through a pore, within which the flow of diffusing substance is restricted by the size of the pore, the layer of previously adsorbed molecules, or can encounter directly the surface of the sphere. This can create a certain mass transfer resistance (Bimbenet *et al.*, 1969), which can be further increased if the sphere is surrounded with a boundary layer of unsaturated liquid as the result of inadequate agitation (movement). Equation (6.4) is not applicable in the case of surface resistance and has to be replaced by a more complex solution (Crank, 1967).

6.4. Application to Potato Granules

6.4.1. Introduction

It is reported in literature (van Arsdel, 1973) that the diffusion resistance factor, ϕ, like the moisture conductivity through water-filled pores, is dependent not only on the geometrical fine structure of the solid material, but also, in hygroscopic materials,

very strongly on the moisture content. Görling's (1958) results on potatoes show an exceedingly steep increase in the diffusional resistance as moisture content falls below about 20% (d.b.). The result of this is a hundred-fold decrease in diffusivity as the moisture content falls from 15% to 3% (d.b.) (Fish, 1958). The rehydration process could be described in terms of a diffusion coefficient which depends on the moisture content of the material. In macromolecular systems there is a wide variation of the diffusion coefficient with the concentration of the solvent or penetrant. It is proposed to limit the change in moisture content in each experimental determination to a small interval, so that it becomes possible to neglect changes in the diffusion coefficient and in the volume of the material. Potato granules have widths of pores (max. ~80 Å) in the range which is well below the range ascribed to macropores (> 200 Å), Gregg and Sing (1967), so the study of diffusivity is less complicated. The study on diffusion and thermodynamics of water in potato starch gel (Fish, 1958) showed that changes in the thermodynamic properties of water in starch gel occur as the moisture content is reduced, especially below 10% on the dry basis. The slow transport of water in dry starchy material is associated with the loss of rotational freedom of the water molecules. The height of the energy barrier for the fundamental process of diffusion appears to increase as the moisture content of the material is reduced.

6.4.2. Methods

6.4.2.1. Determination of diffusion coefficient

In order to determine which equation should be used for the determination of D the resistance at the surface of F-T potato granules

was tested using the values of $(\frac{m - m_0}{m_\infty - m_0})$ for the potato granules with an initial moisture content of 3.59%, 5.23%, 7.88% and 9.95%. These were plotted against $(\frac{D\theta}{r^2})^{\frac{1}{2}}$ on a graph along with the theoretical sorption or desorption curves for the surface condition $-D \frac{\partial c}{\partial r} = \alpha(C_s - C_0)$ (Crank, 1967), where C_0 is the concentration required to maintain equilibrium with the surrounding atmosphere, C_1 is initial concentration of the sphere and C_s is the actual concentration just within the sphere. Numbers on theoretical curves (Fig. 28) are values of $L = \frac{r\alpha}{D}$, where α is the mass transfer coefficient.

During the early stages of the diffusion process, when the moisture content within the starch granules is not appreciably altered, the change in weight $(\frac{m - m_0}{m_\infty - m_0})$ of the granule varies as the square root of the time $(\sqrt{\theta})$ (Fish, 1958).

Adsorption data from Fig. 34 expressed as kg water/kg wet material were transformed in % on dry basis (Table 8) and plotted as $\frac{m - m_0}{m_\infty - m_0}$ against $\sqrt{\theta}$, where m_∞ = 32.90% dry basis (experimental).

In the case of potato granules, equation (6.4) was reduced to its first time for long times and leads by taking the logarithm of both sides and rearranging to:

$$\ln \left(1 - \frac{M_t}{M_\infty}\right) = \ln \frac{6}{\Pi^2} - D\Pi^2\theta/r^2 \qquad (6.4.1)$$

or

$$\ln \left(1 - \frac{m - m_0}{m_\infty - m_0}\right) = \ln \frac{6}{\Pi^2} - \frac{D\Pi^2\theta}{r^2} \qquad (6.4.2)$$

where:

m_0 = initial moisture content of potato granules in % (d.b.)

m = moisture of potato granules in % (d.b.) being adsorbed for a certain time at R.H. = 100% and t = 23°C

m_∞ = experimental value for maximum adsorbed moisture by potato granules kept at R.H. = 100% and t = 23°C until equilibrium was reached

D = diffusivity coefficient in $m^2 s^{-1}$

θ = time in seconds (s)

r = maximum average radius of potato granules (= 50μ = 5×10^{-5}m)

Plotting $(1 - \frac{m - m_0}{m_\infty - m_0})$ against θ on semilogarithmic paper for F-T potato granules with initial moisture contents 3.59%, 5.23%, 7.88% and 9.95% and taking into consideration a linear portion of the curves, the slopes (S) can be calculated and using the relation

$$S = - \frac{D\Pi^2}{r^2} \qquad (6.5)$$

diffusion coefficient D can be obtained.

$$D = -2.3026 \frac{r^2 S}{\Pi^2} \qquad (6.6)$$

6.4.2.2. Determination of rehydration rate of potato granules

A. The first method was a simulation of the reconstitution process as used in the manufacture of the extruded french fries. Potato granules were fed slowly through a glass funnel into tap water which was being vigorously stirred with a magnetic stirrer. The process was carried out in a 600 ml glass beaker; 30 g of potato granules were fed into 62.4 ml water at 19°C in about 12 sec. The time taken from the first contact of the granules and water until the 3 inch magnetic stirrer stopped moving, represented a measure of the rehydration time of the granules and was expressed in seconds.

B. In the second method, Petrie dishes were used as containers. A very thin layer of potato granules was placed into the

dish and weighed. The bottom section of the desiccator was filled with water and the sample placed in the desiccator at constant temperature (23°C); the atmosphere in the desiccator was considered 100% RH. The sample was weighed at certain time intervals and the rehydration expressed as kg water per kg wet material. The results were plotted as kg water per kg wet material vs time in seconds.

6.4.2.3. Structural rearrangement as analyzed by differential thermal analysis (DTA)

A three unit Differential Thermalyzer, consisting of a Model 260P Programmer, a Model 260F Furnace and a sample holder provided with an Inconel Block (Fisher Scientific Instrument Division, Pittsburgh, Pa.) and a mV dual channel strip-chart recorder (Yokogawa, Type 3047) were used.

Dilution of the samples of potato granules with aluminum oxide, 100-200 mesh in size, was necessary in order to prevent mild explosion which occurs at the temperatures between 270° and 320°C and dislocate the thermocouple from the sample. This procedure was suggested by Morita and Rice (1955), Varma (1958) and Mackenzie and Mitchell (1972). The dilution in the ratio of sample: Al-oxide = 3:4 was found to offer maximum sensitivity without the explosion. The samples were thus thoroughly mixed with the alumina before packing into the sample crucibles.

The furnace chamber was first flushed with nitrogen before the sample holder was placed in the position. During the operation the chamber was continuously flushed with 3 ℓ/min of nitrogen.

The heating was programmed at the rate of 10°C/min. The heating curve and the thermogram of the sample were recorded on the Yokogawa

dual recorder. Aluminum oxide (anhydrous), 100-200 mesh, was used as the reference material. The DTA was standardized using calcium oxalate as the sample. To ascertain the inertness of aluminum oxide (anhydrous), its thermogram was also obtained under the standardized conditions. The signal output was 0.5 mV and the recorder chart speed was 0.555×10^{-4} m/s (0.20 m/hr)

6.4.3. Results

6.4.3.1. Effect of water content of the granules on diffusivity

Figure 28 shows the theoretical and experimental sorption curves for the surface condition $-D \frac{\partial C}{\partial r} = \alpha(C_s - C_0)$. The experimental sorption curves were obtained by plotting the values of $(\frac{m - m_0}{m_\infty - m_0})$ against $(\frac{D\theta}{r^2})^{\frac{1}{2}}$ on a graph along with the theoretical sorption curves (L). This was necessary in order to determine right equation for the determination of D. All experimental sorption curves fell very close to the theoretical curve $L = \infty$. Consequently the simpler form of equation (6.4) can be used to calculate D (6.4.2).

In order to determine the characteristic of diffusion in the potato granules, the change in weight $(\frac{m - m_0}{m_\infty - m_0})$ of the granules was plotted against square root of time $(\sqrt{\theta})$. The curves (Fig. 29) are characteristic of diffusion in potato starch gel with a moisture content of less than 15%. As it was mentioned earlier, Fish (1958) reported that the coefficients for diffusion of water in scalded potato and potato starch gel are function of moisture content and they increase with the change of moisture from 3 to 15% dry basis. At the same ambient relative humidity, the moisture content in a sample of scalded potato will be less than that in pure starch gel because of the other

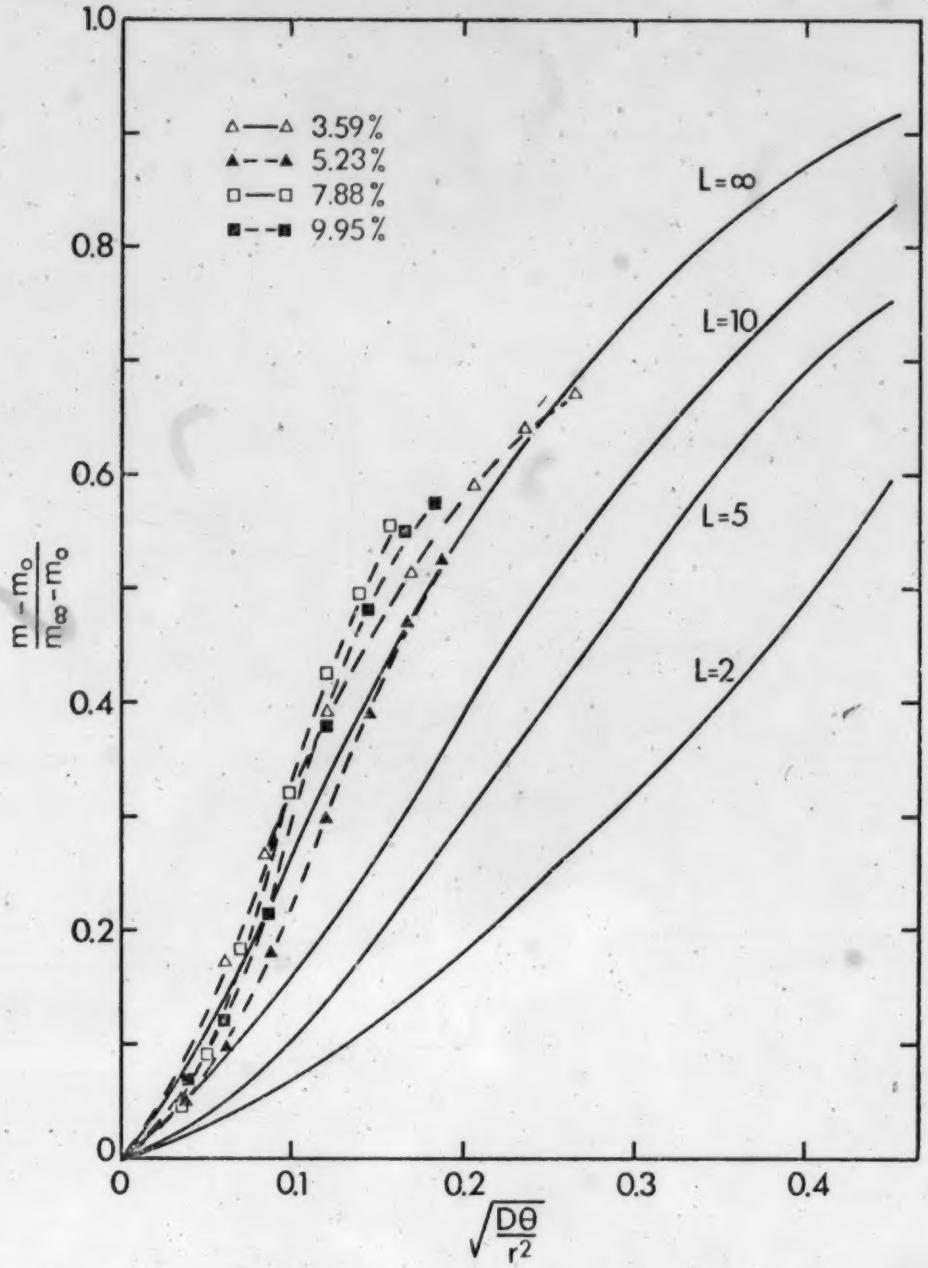


Fig. 28. Theoretical and experimental sorption curves for the surface condition $-D \frac{\partial c}{\partial r} = \alpha(C_s - C_o)$. Numbers on theoretical curves are values of $L = r\alpha/D$.

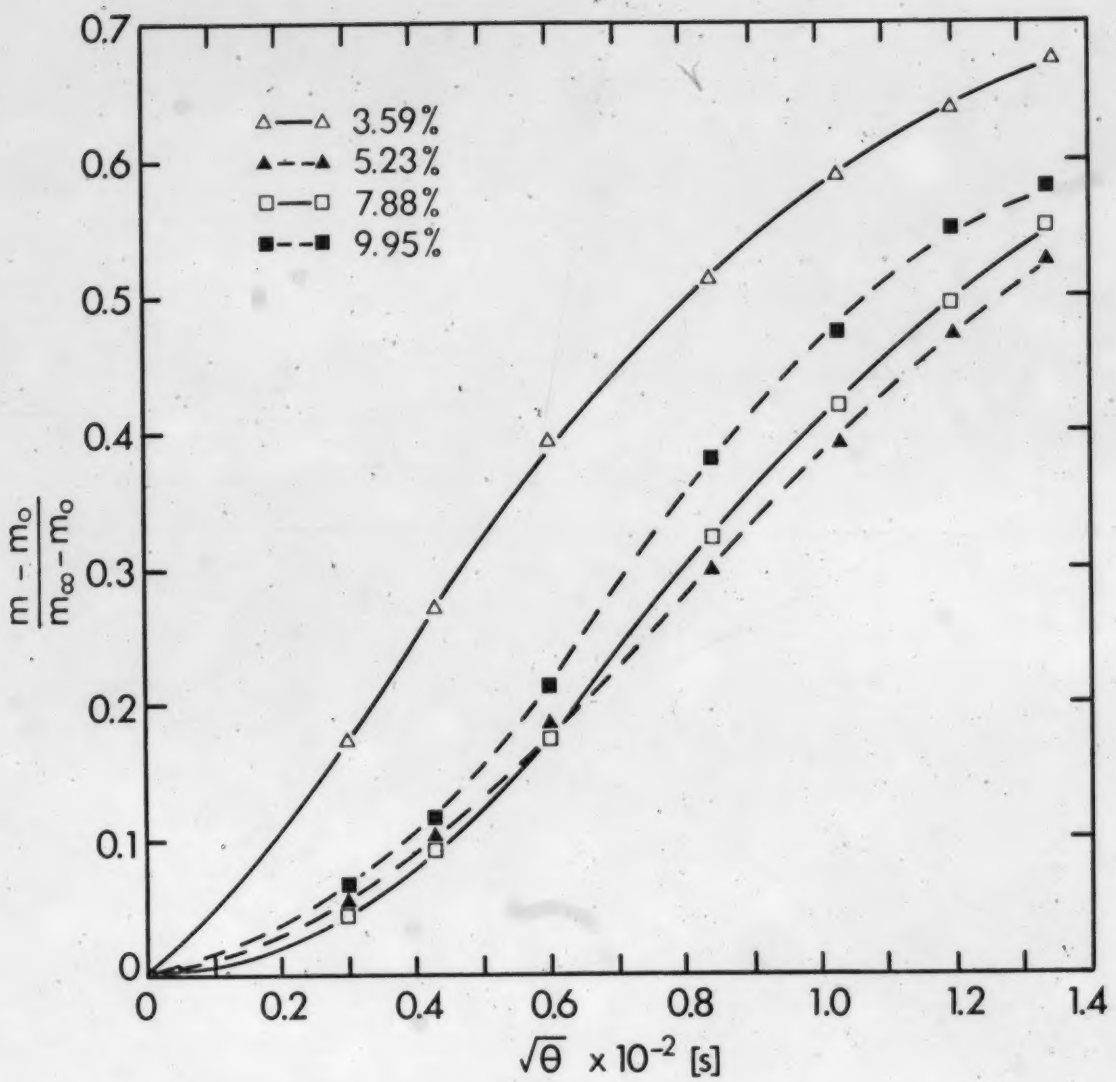


Figure 29. The relationship between the total amount of diffusing substance (water) entering the granule and square root of the time.

components in potato. This may account for the sigmoid shape of the curves (Fig. 29).

Another factor which could also play a very important role in the diffusion of water in potato granules is the shrinkage of solid porous granules during dehydration. A change of capillary and pore diameters is to be expected.

Diffusion coefficients D of the potato granules were obtained using formula (6.6), where S represents the slope of the curve. The curves (Fig. 30) are the result of the plot $(1 - \frac{m - m_0}{m_\infty - m_0})$ against Θ on semilogarithmic paper (see equation 6.4.2). The slopes were calculated from a linear portion of the curves (from $\Theta \geq 7.2 \times 10^3 s$).

The following average diffusion coefficients were calculated:

$\bar{D}_1 = 0.22 \times 10^{-13}\ m^2 s^{-1}$ for 3.59% (3.72% d.b.)

$\bar{D}_2 = 0.21 \times 10^{-13}\ m^2 s^{-1}$ for 5.23% (5.51% d.b.)

$\bar{D}_3 = 0.26 \times 10^{-13}\ m^2 s^{-1}$ for 7.88% (8.55% d.b.)

$\bar{D}_4 = 0.29 \times 10^{-13}\ m^2 s^{-1}$ for 9.95% (11.04% d.b.)

The results showed an insignificant change of the diffusion coefficient with the change of inital moisture content of the material through which diffusion occurred. The results from the literature (Fish, 1958) where the experiments were conducted on potato starch gel and scalded potatoes with initial water contents from 3.5% to 10%, showed the change of D in the range of 0.1×10^{-13} to $0.3 \times 10^{-11}\ m^2 s^{-1}$.

There exists a very close agreement with the literature results only for initial moisture content of 3.5%.

From the pore size analysis (5.3.1.4) it appears that the granules are predominantly microporous and therefore there is a small chance that water penetrates through them. If this happens to some extent then it

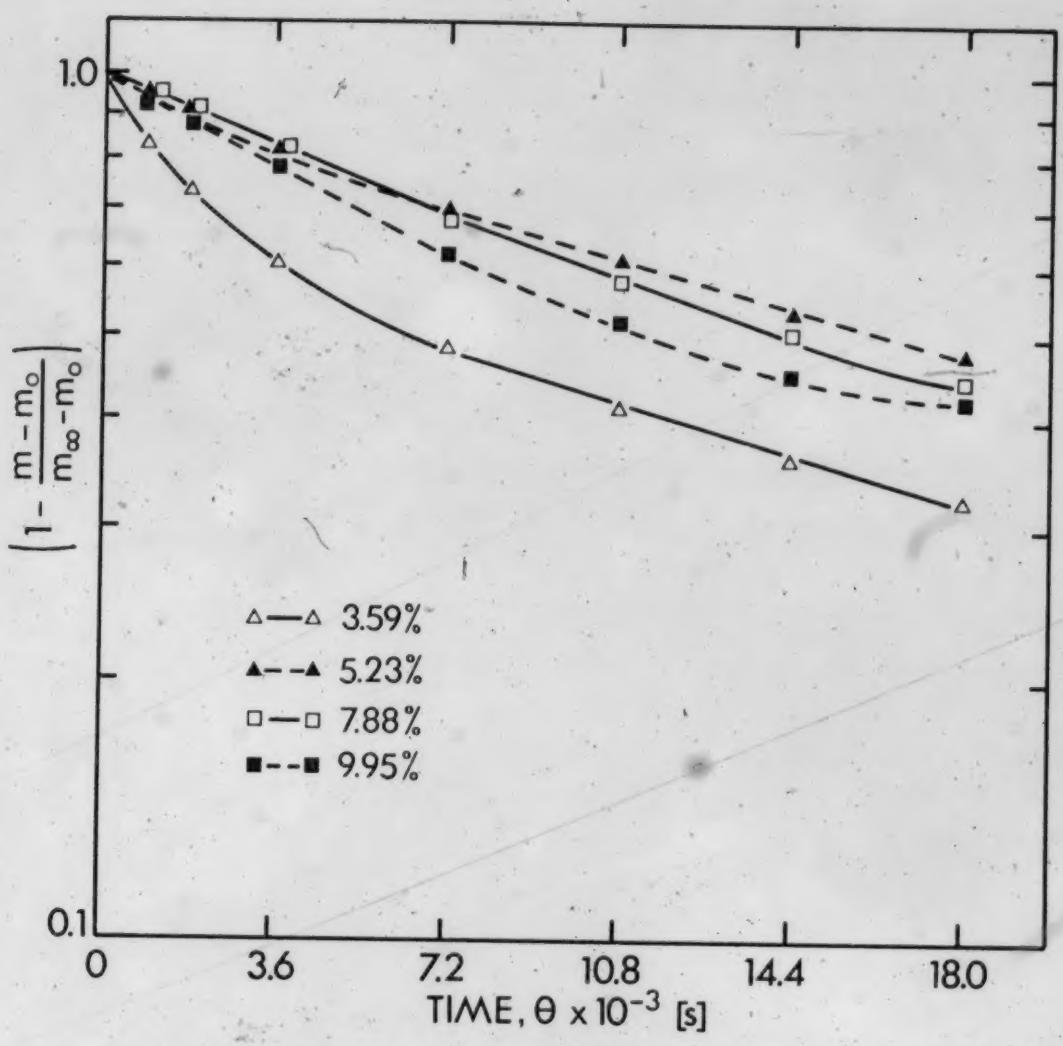


Figure 30. Sorption curves obtained using formula (6.4.2) in order to calculate diffusion coefficients (see Table 7 and Fig. 34).

means that water penetrates the transitional pores (10 Å < r < 100 Å) possibly by dissolution or absorption in the gelatinized starch. Due to predominant presence of micropores the mechanism of diffusion of water into potato granules generally could be considered one of solid diffusion.

The reason for the discrepancy of the results from the literature and from this work might be also in the method of obtaining the data for the calculation of D. In the literature an attention is given to the difference in partial pressure of water vapor between the surface of the specimen and the solution which determines RH (acid). This difference depends on the efficiency of the transport process across the air-solid interface. In order to study diffusion of water through the solid uninfluenced by diffusion through the air, it is necessary that this difference in partial pressure is small enough to be negligible. Any errors due to the transport of water through the ambient air will be greatest at the high rates of transport which occurs during the initial stages of diffusion. This becomes apparent when very thin films of material are studied. Therefore an evacuated sorption balance has been suggested and water vapor is admitted to the evacuated space from the vessel which contains outgassed solution (acid).

Saravacos (1967) reported the results on D of dehydrated potatoes by freeze-drying, air drying and puff-drying, as the apparent diffusivity which is a better approximation. He used the same initial formula as it was done in this work. The apparent diffusivity was defined as equal to $(D_s + D_d)/2$ where D_s and D_d were calculated from the half-equilibrium time for adsorption and for desorption. The results showed that D increased slightly from 0.2×10^{-11} to 1.0×10^{-11} $m^2 s^{-1}$ with

the increase of moisture content of the sample from 3.5% to 10% for air-dried potatoes. For freeze-dried potatoes, D was much higher (magnitude of 10^{-9}; due to water being transferred by a combination of diffusional and hydrodynamic flow) and decreases with an increase of moisture content.

It is obvious that anomalies exist as far as diffusivity is concerned, and they are recognized as the illogical ones and could be resolved to a large extent by a mathematical analysis of the mechanisms and interaction of heat and mass transfer in the sorption and drying process (King, 1968). The two processes, the transfer of moisture and the transfer of heat, are occurring simultaneously, and cannot in general be considered separately. Namely, during diffusion, changes of moisture content may be accompanied by a considerable exchange of heat. This heat will diffuse through the medium towards the outside and will affect the extent to which moisture can be absorbed.

6.4.3.2. Effect of uncontrolled atmosphere on rehydration of the granules

Newly processed freeze-thaw (F-T) potato granules (from the same batch) were stored at room temperature for 1, 2, 3 and 12 months and the rehydration rate of these granules was determined. To determine the rate of rehydration, two methods were chosen. In the first method, potato granules were fed slowly into tap water which was being stirred vigorously. The time taken from the first contact of the granules and water until stirring stopped due to the formation of dough was taken as the time of rehydration and was expressed in seconds. The amount of granules and water used was determined from the ratio of water:granules $\simeq$ 2:1, since dough for french fries is produced by

rehydrating potato granules in cold water in the same ratio. In Table 4 the time of rehydration of potato granules, stored for certain times, is shown. There were three determinations for each sample and the average rehydration time along with the standard deviation was calculated. The rehydration time increased as the storage time increased. In the second method, the weight increase of the granules (kept under the condition of 100% RH) due to the water adsorption was measured against time. The results were plotted as kg water per kg wet material versus time in seconds (Fig. 31).

As the storage time increased, the rate of rehydration decreased, such changes being most prominent on those granules being stored for three months and over. The rate of rehydration was expressed as the initial rate of rehydration given in kg water per kg wet materials, and it was measured by the slope of the tangents at the origin of the curves (Table 5). The term kg wet material corresponds through all experiments to the granules with an initial water content.

Newly processed granules were stored at room temperature in flexible packages which were neither tightly sealed nor impermeable. Under these conditions there exist a possibility that the granules, which possess a high amount of starch known for its water holding capacity, adsorb (or desorb) certain moisture depending on storage conditions (relative humidity, RH and temperature, t). From Figure 31 and Table 5 we can see that the monolayer capacity of the F-T granules, around 5.4% (Table 2) is exceeded after a three-month storage period.

Water in excess of the monolayer is picked up by the granules, and is thought to be hydrogen bonded between hydroxyl groups on adjacent starch chains or on the same coiled chain. This can be attributed to

Table 4: The Rehydration of Potato Granules Stored for Different Periods of Time at Room Temperature

Sample	Storage Time Months	Time of Rehydration, sec			
		1	2	3	Ave.
1	0	13.0	12.8	12.9	12.9 ± 0.1
2	1	15.0	15.3	15.3	15.2 ± 0.2
3	2	15.8	16.1	15.8	15.9 ± 0.2
4	3	17.0	16.5	16.6	16.7 ± 0.3
5	12	19.5	19.6	19.0	19.4 ± 0.3

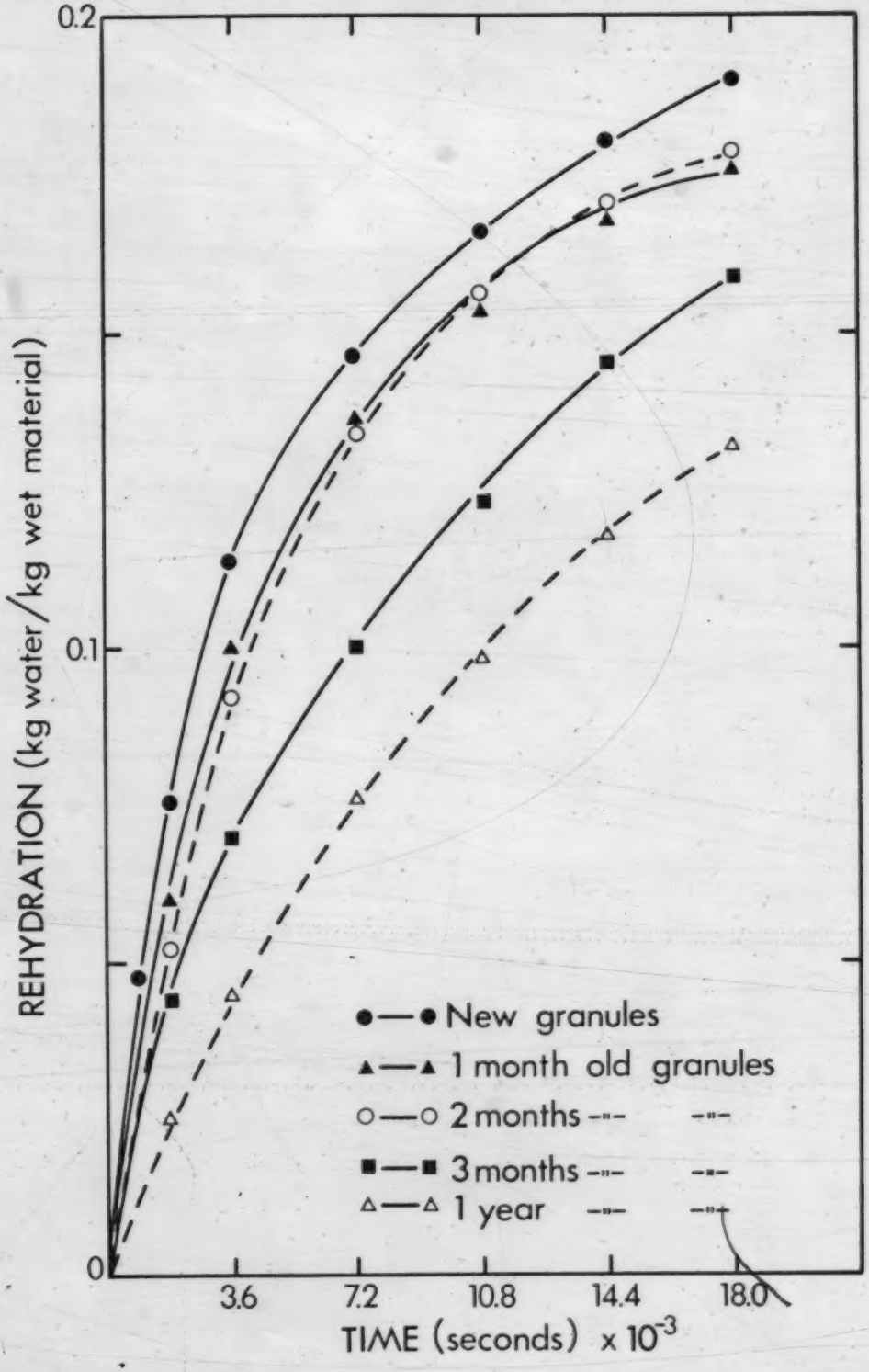


Figure 31. Effect of ageing on the rate of rehydration of F-T potato granules.

Table 5: Influence of Storage Time of the Granules at Room Temperature (see Fig. 31 and Table 4) on Moisture Content and Rate of Rehydration of F-T Granules

Sample	Average Wet Basis Moisture Content in %	Rate of Rehydration kg water/ (kg wet material·s)
New granules	4.76	3.17×10^{-5}
1 month old granules	5.25	2.78×10^{-5}
2 month old granules	5.82	2.56×10^{-5}
3 month old granules	7.06	1.94×10^{-5}
1 year old granules	8.91	1.22×10^{-5}

the fact that each anhydroglucose unit contains 5 groups--three OH groups and two oxygen atoms which together provide 13 possible hydrogen bonding sites (Fig. 32).

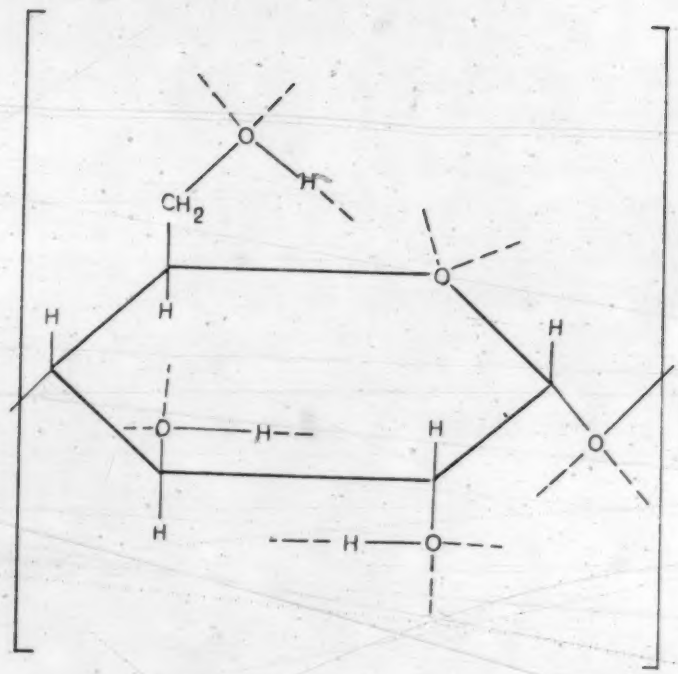
According to Collison and Dickson (1971) and Guilbot *et al.* (1960) the restrictions are inevitable due to steric and other factors leaving only limited number of the H-bonding sites.

In the storage room the existing conditions of 42-51% RH and 21.5-24.5°C resulted in an increase of moisture content with time (Table 5). This evidence suggests a possibility of water interference with readsorption characteristics of potato granules.

In the second set of experiments, the moisture content as well as the rate of rehydration of new granules processed by the freeze-thaw technique, new granules processed by the add-back process and commercial french fry mix were determined. The rates of rehydration of these products are shown in Figure 33. The results obtained are an average of three determinations. The difference in the rate of rehydration between these three products is obvious and the analysis of their moisture contents (Table 6) showed differences and thus it was decided to investigate more thoroughly the influence of moisture content upon rehydration rate.

6.4.3.3. Effect of controlled atmosphere on rehydration of the granules

Freshly processed potato granules by the F-T technique were exposed to atmospheres of different relative humidities until equilibrium was reached (Table 7). Equilibrium was reached after six days for most of the samples. Figure 34 shows the rates of rehydration of the F-T potato granules stored at various relative humidities. Plotting



(Collison and Dickson, 1971)

Figure 32. The potential hydrogen bonding sites of the anhydroglucose unit of starch.

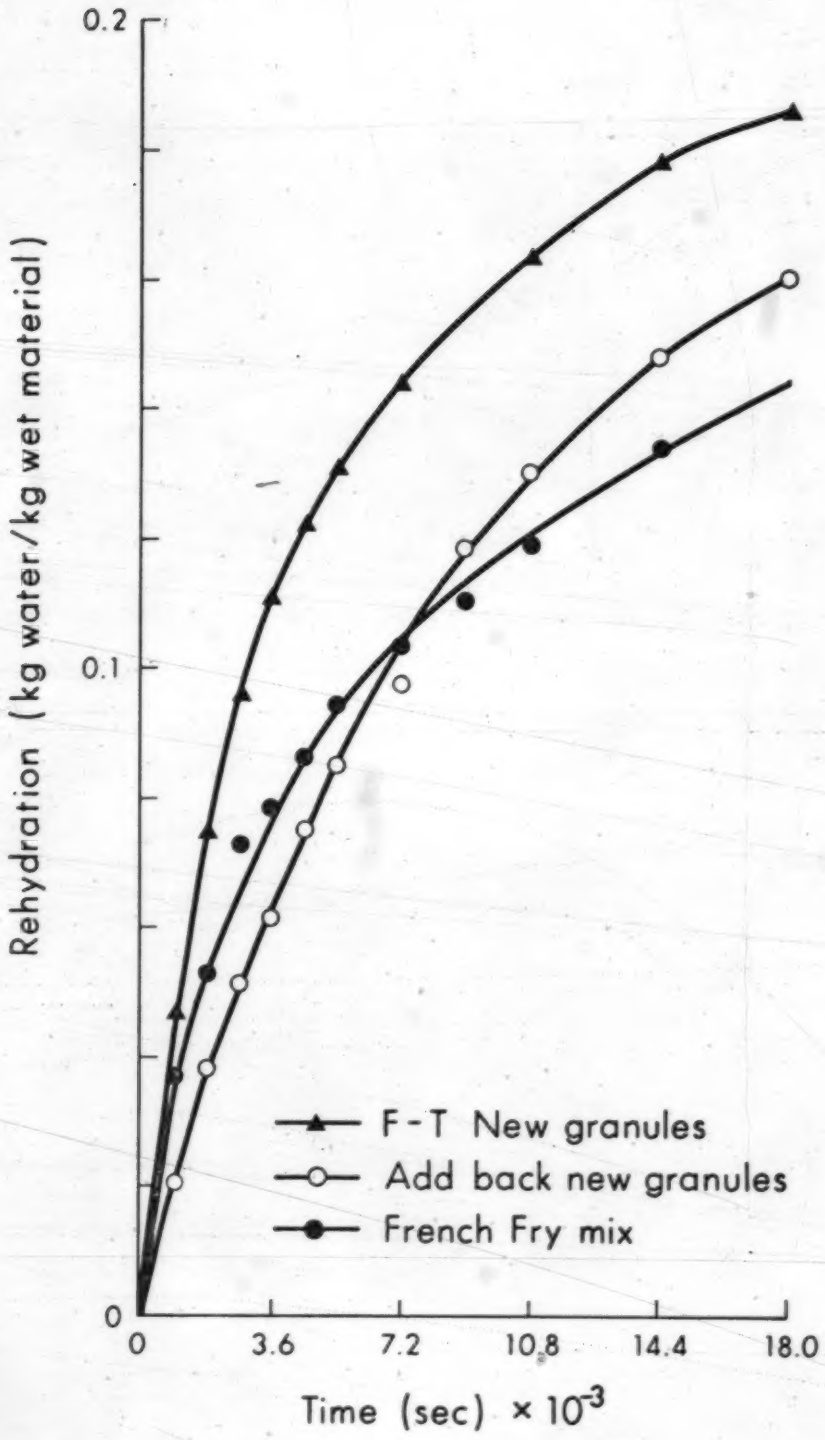


Figure 33. Rate of rehydration of different potato granules.

Table 6: Average Initial Moisture of Different Granules Related to Their Rate of Rehydration

Product	Initial Wet Basis Moisture Content in %	Rate of Rehydration kg water/ (kg wet material·s)
F-T granules	4.94	3.6×10^{-5}
French fry mix	7.49	1.7×10^{-5}
Add-back granules	8.12	1.6×10^{-5}

Table 7: Moisture Sorption Isotherms: Data for Adsorption of New Potato Granules by Freeze-Thaw Technique (F-T)

Temperature: 23°C

Adsorption		
ERH %	Equilibrium Wet Basis Moisture Content in %	kg Water/ 100 kg dry Solids
0	3.59	3.72
11.1	5.23	5.51
32.9	7.88	8.55
51.8	9.95	11.04
75.5	13.34	15.39
86.5	15.59	18.47
100	24.74	32.90

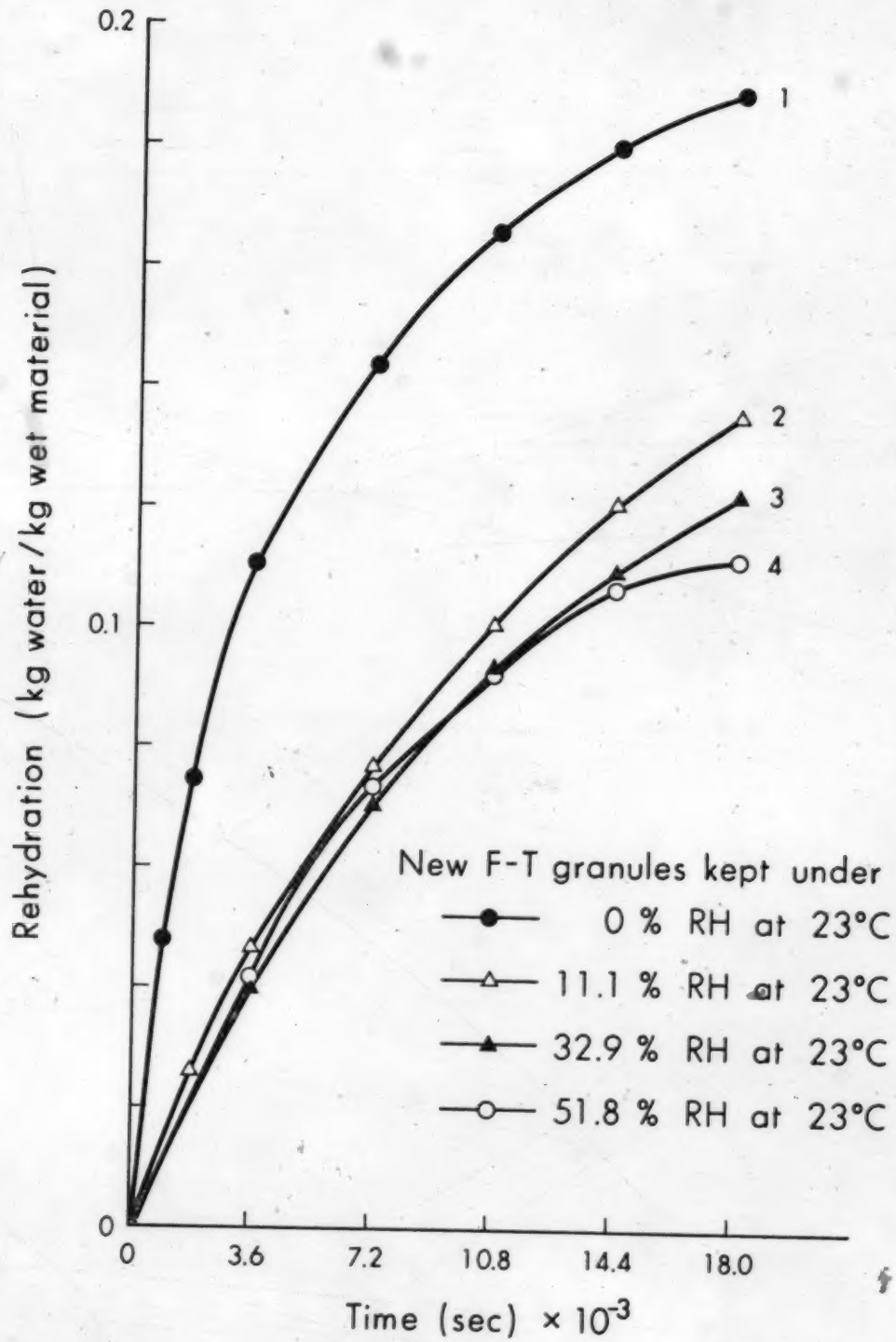


Figure 34. The rehydration rate of F-T potato granules stored at different relative humidities.

the initial rate of rehydration of the curves from Figure 34 (new granules under storage conditions of different RH at constant temperature) versus water activity a_w (ERH/100), we were able to see more explicitly the sudden drop in the rate of rehydration as a function of increased a_w in the range from 0 to 0.111. Beyond that point there was no significant change according to data obtained (Fig. 35). The point 0.295 on the ordinate represents the rate of rehydration of the granules kept under the atmosphere of $a_w = 0.0$ (the sample kept above P_2O_5) and showed the same rate of rehydration as the newly processed granules. The line at 0.132 on the ordinate represents the rehydration rate of 1-year old granules, and is used for comparison since these granules are considered suitable for making french fry mix.

Although the curves (Fig. 34) differ from each other at the initial stage of rehydration, all of them should reach the same equilibrium value which was found for this particular case to be $Y_e = 32.90\%$ dry basis (db) (Table 7). The determination of an equilibrium value is time consuming when transient state values slowly converge to an equilibrium state and this determination is almost impossible when sample material deteriorates biologically, chemically and/or physically during experimentation. Equilibrium values are frequently required for kinetic analyses of some processes. In this study the equilibrium moisture was needed for determining the diffusivity of water in the sample material or for predicting the rate of moisture sorption.

Following a technique described by Hayakawa (1974), the time necessary to reach equilibrium and the maximum quantity sorbed can be determined. For predicting equilibrium values Hayakawa suggested the use of three equations:

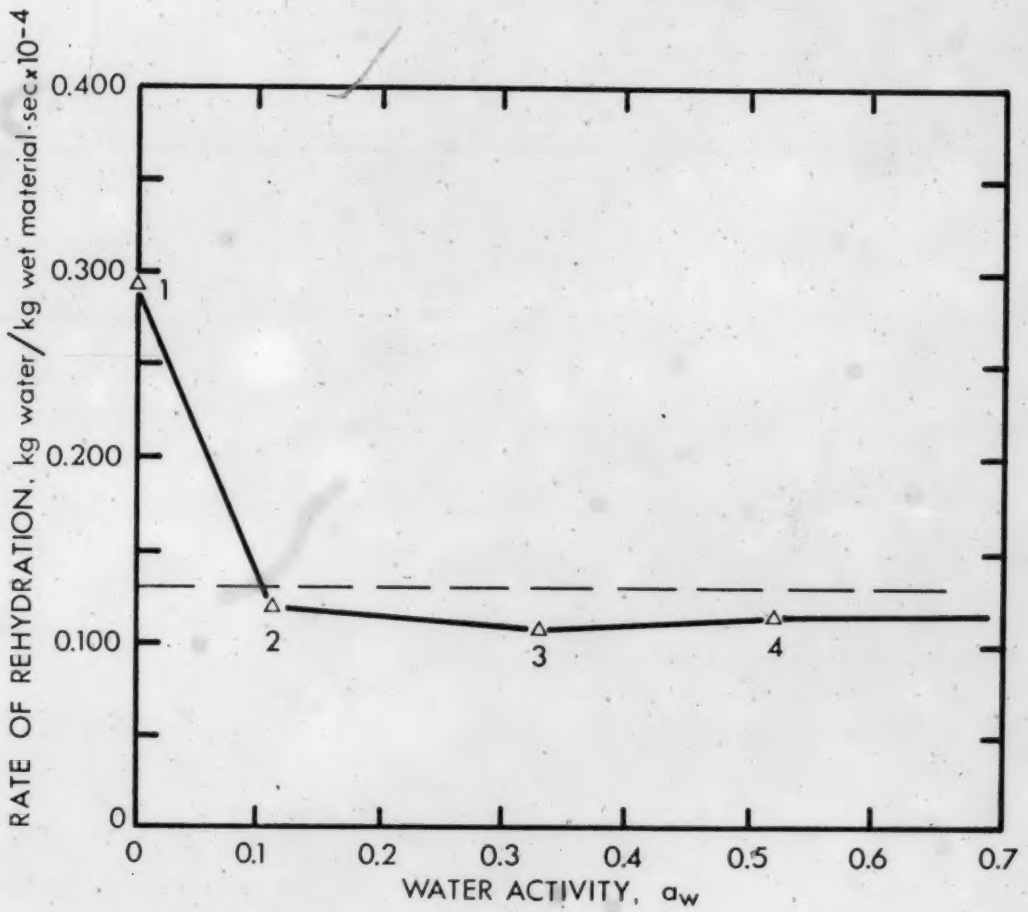


Figure 35. The initial rates of rehydration taken from the curves of Fig. 34 versus water activity a_w.

$$s = \frac{D}{\log[(Y_i - Y_{i-1})/(Y_{i+1} - Y_i)]} \qquad (6.7)$$

$$b = \frac{(Y_i - Y_{i-1})}{10^{-t_{i-1}/s}(10^{-D/s} - 1)} \qquad (6.8)$$

$$Y_e = Y_i - b.10^{-t_i/s} \qquad (6.9)$$

where: s = a constant equivalent to the time t required for a line on a semilogarithmic paper to traverse one log cycle. Semilogarithmic curve in this case could be obtained by plotting the common logarithms of differences between transient (Y) and equilibrium (Y_e) state values ($Y - Y_e$) against value of t.

D = uniform intervals of t at which Y values are estimated.

b = constant which represents an intercept coefficent of a line segment of a semilogarithmic curve on the ordinate ($Y - Y_e$).

Y_e = equilibrium state value of Y.

In Table 8, transient state data used in the sample from Figure 34 are shown. Data represent the change of moisture sorption (calculated in % dry basis) against time in hours, and their corresponding rate of moisture and ratio of the rates. According to Hayakawa (1974) three requirements should be satisfied in order to predict accurately Y_e values.

A. $(Y_i - Y_{i-1})/(Y_{i+1} - Y_i) \neq 1$

B. A value of D should be less than one-third of an s value

C. Transient state Y values should be collected until the following condition is satisfied

Table 8: Transient State Data Used in a Sample. Moisture Adsorption of F-T Potato Granules with Initial Moisture Content 3.59%

Time (hr)	Moisture (% dry basis)	Rate of Moisture Rate	Rate of Moisture Ratio
0	3.72		
1	15.23	11.51	1.00
2	18.66	3.43	0.30
3	20.94	2.28	0.20
4	22.40	1.46	0.13
5	23.33	0.93	0.08

t_i = 2 hr

$$s = \frac{1}{\log[(18.66 - 15.23)/(20.94 - 18.66)]}$$

$s = 5.64$ hr

$$b = \frac{3.43}{[10^{-1/5.64}(10^{-1/5.64} - 1)]}$$

$b = -15.29$

$Y_e = 18.66 - (-15.29)10^{-2/5.64}$

$Y_e = 25.34\%$ dry basis

$(Y_{i+1} - Y_i) \cdot D \simeq 0.2 \cdot R_{max}$, where R is the rate of change in Y values

Similar calculations were done for the granules with initial moisture content of 5.23%, 7.88% and 9.95% and the following values of Y_e were obtained:

Y_e = 25.92% for 5.23%

Y_e = 29.05% for 7.88%

Y_e = 27.61% for 9.95%

The average value was calculated

$\overline{Y}_e$ = 26.98% db

which comparing to the experimental value Y_e = 32.90% db (Table 7) could be considered satisfactory.

6.4.3.4. Effect of storage on rehydration of the granules

In order to prevent any influence of uncontrolled atmosphere on the granules, the granules from the same batch with initial moisture content of 6.55% were stored for 7, 30 and 60 days under the atmosphere of $a_w = 0 (P_2O_5)$, $a_w = 0.329 (MgCl_2)$ and $a_w = 0.518$ $(Ca(NO_3)_2)$ at constant temperature t = 23°C. Moisture content and the rate of rehydration were determined after each of the three storage periods.

Storage under $a_w = 0 (P_2O_5)$: Figure 36 shows the rates of rehydration of the granules kept under $a_w = 0$ for 7, 30 and 60 days at t = 23°C. The rate of rehydration increased after 30 days of controlled storage, compared to the granules kept for 7 days under the same storage conditions. Since moisture content decreased (Table 9), the increase in the rate of rehydration was likely due to a decrease in moisture content. After 60 days the rate of rehydration decreased but moisture

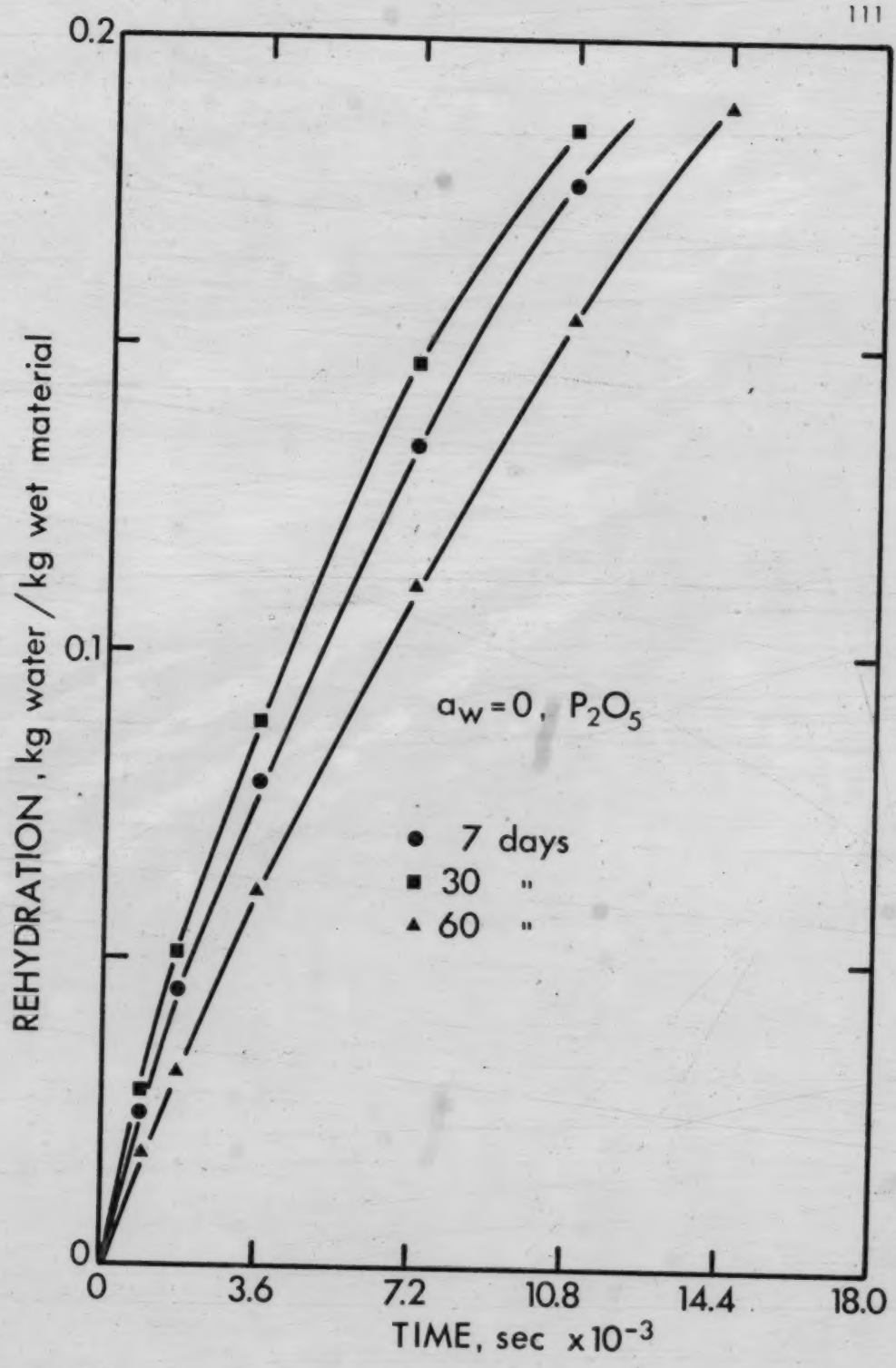


Figure 36. Effect of the controlled storage (a_w = 0) on the rate of rehydration of F-T potato granules.

Table 9: Influence of Storage Conditions on Moisture Content of the Granules During the Storage Period

Storage Conditions	Moisture Content (%) Time of Storage in days		
	7	30	60
a_w = 0	2.17	1.51	1.51
a_w = 0.329	7.51	7.49	7.46
a_w = 0.518	10.01	9.86	9.83

content of the sample did not change.

Storage under $a_w = 0.329 (MgCl_2)$: Figure 37 shows the rates of rehydration of the granules kept under $a_w = 0.329$ for 7, 30 and 60 days at $t = 23°C$. There was no significant change neither in the rate of rehydration nor in the moisture content after 30 and 60 days of the storage (Table 9).

Storage under $a_w = 0.518 (Ca(NO_3)_2)$: Figure 38 shows the rates of rehydration of the granules kept under $a_w = 0.518$ for 7, 30 and 60 days at $t = 23°C$. The moisture content increased to 10.01% in 7 days. In the following 23 days there was no significant change in moisture content neither was any change of moisture content after 60 days of the storage (Table 9). The rate of rehydration increased after 30 days and decreased after 60 days of the storage.

In this experiment as in the previous one (storage under $a_w = 0$) the change in the rate of rehydration occurs likely due to the molecular rearrangement which might take place during the storage. To explain this the following could be offered: In the first case an excessive drawing of the moisture from the sample could result in the creation of "empty space" among the large molecules. The molecules would come closer to each other and this would bring about a restricted penetration of water molecules into the molecules of potato granules during the rehydration. In the second case (storage under $a_w = 0.518$) it appears that the presence of the increased amount of water could initiate some molecular rearrangements which could bring about the change of the rate of rehydration (French, 1950; Potter, 1954).

Chilton and Collison (1974) suggested that the maximum uptake of moisture requires time to allow for some molecular rearrangement within

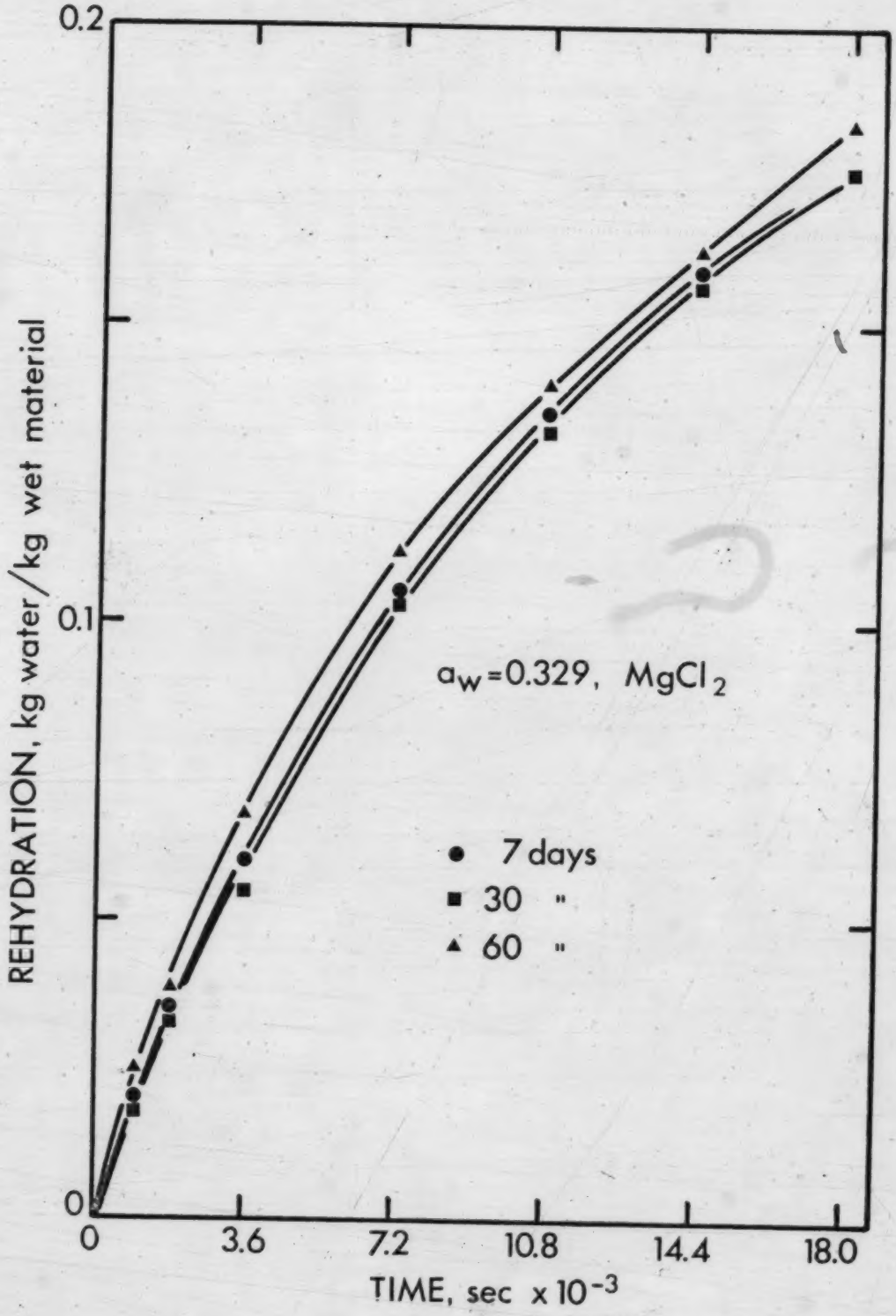


Figure 37. Effect of the controlled storage (a_w = 0.329) on the rate of rehydration of F-T potato granules.

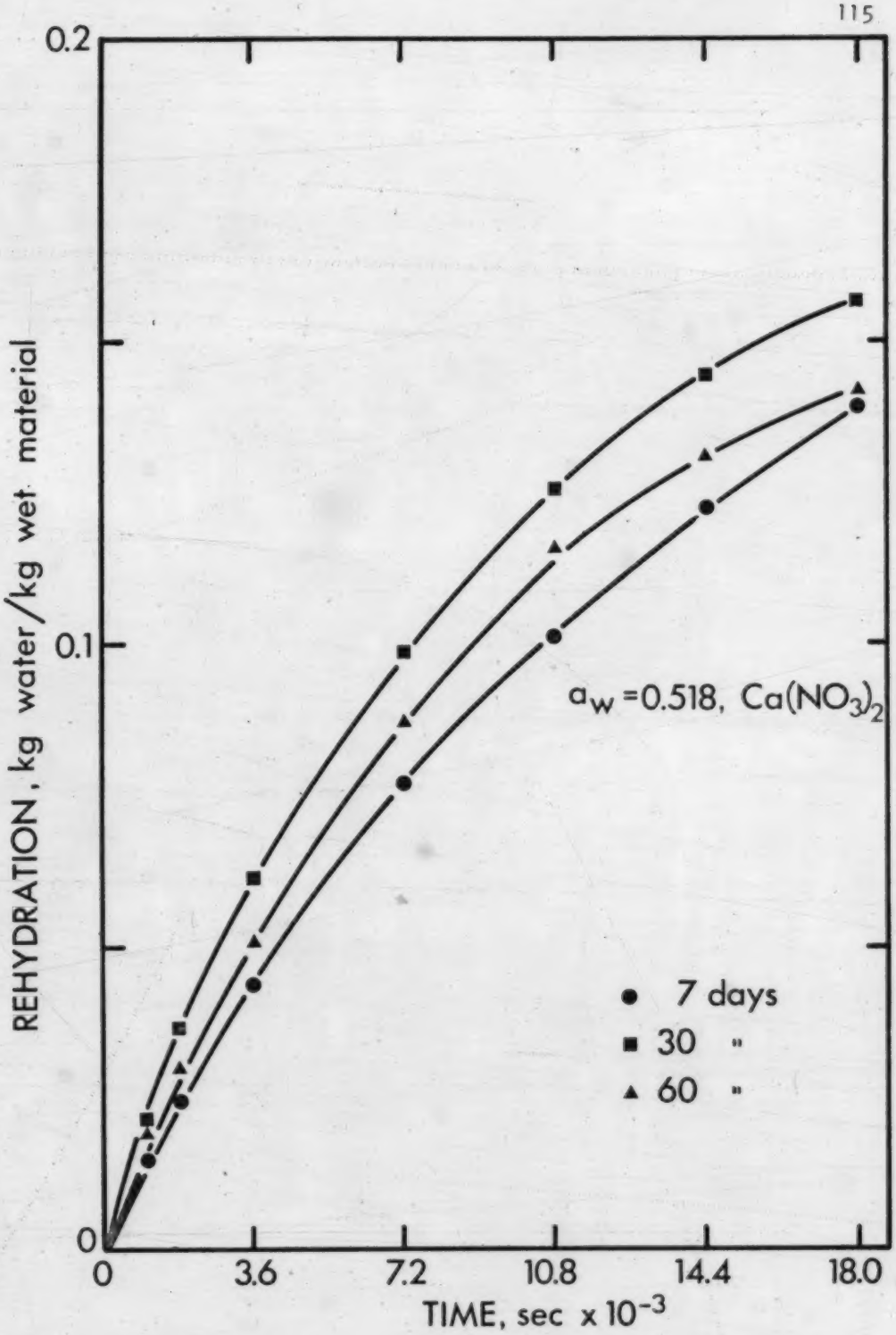


Figure 38. Effect of the controlled storage (a_w = 0.518) on the rate of rehydration of F-T potato granules.

starch granules. This is supported by an evidence which strongly suggests that water molecules are distributed at sites throughout the granule and are not restricted to the surface (Hellman and Melvin, 1950).

The differential thermal analysis (DTA), which is known as a very useful technique and has been used to study structural properties of starch, protein and other organic compounds was applied in this case. Newly processed F-T potato granules and one year old granules (from the same batch) were subjected to the DTA. In Figure 39 the thermograms of Ca-oxalate, old F-T granules, new F-T granules and pregelatinized starch are shown. The thermogram of Ca-oxalate served as an aid in identification of the endothermic peaks. Ca-oxalate has two characteristic endothermic peaks at 250°-260° and 500°C (Garn, 1965). In our case, these peaks were at 300° and 575°C. This shift of the apparent reaction temperatures towards higher values might be due to the sample being packed too tightly resulting in the slow diffusion of gasses involved in the reactions. The first endotherm represents loss of water from the compound. The second endotherm at 575°C represents the formation of carbon monoxide by the decomposition of the oxalate. The pregelatinized starch was selected in order to help in analyzing the results of DTA thermograms of the granules due to the fact that the starch in the granules had undergone gelatinization during F-T process. From the thermograms of the granules and pregelatinized starch it appears that the major difference between the thermograms of new and old F-T granules is between 210° and 400°C. New granules exhibit more endothermic peaks in this temperature range than do old granules. There are four endothermic peaks and one prominent exothermic peak common to both

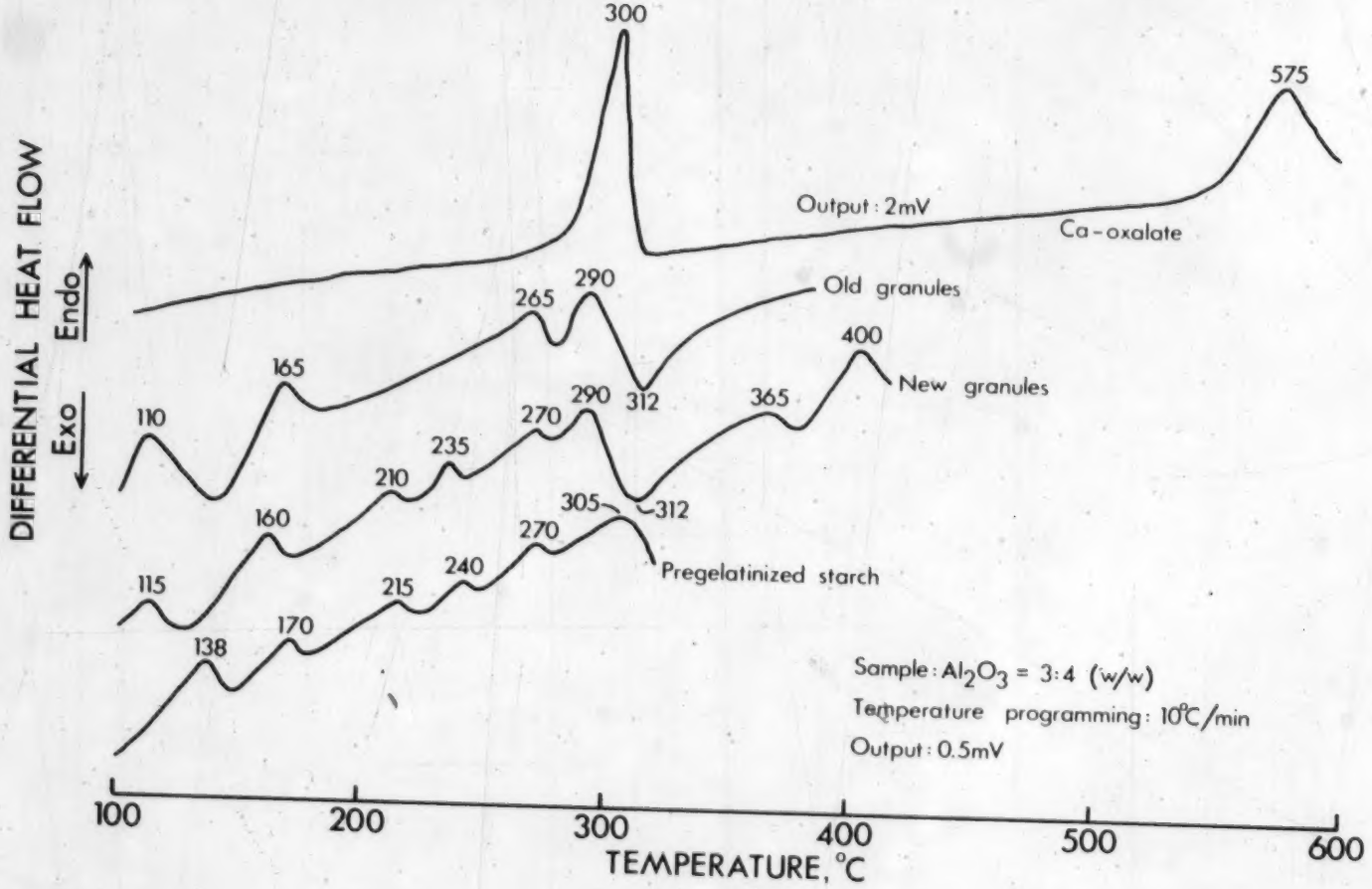


Fig. 39. Thermal curves of old and new F-T potato granules and pregelatinized potato starch.

thermograms, and new granules produce four additional peaks at 210°, 235°, 365° and 400°C. This difference is thought to be due to the fact that during storage (aging) the chemical components in potato granules undergo molecular rearrangement or interreaction. For instance, the unretrograded starch undergoes gradual retrogradation losing some of its molecular water to other components while the starch chains are brought closer together and bound more firmly by hydrogen bonds. Firmer binding may cause resistance to physico-chemical changes which could be initiated by heat during DTA, and result in the thermogram being similar to that of one year old granules.

The thermogram of pregelatinized potato starch from Figure 39 has most of the peaks (170°, 210°, 235° and 270°C) matching those of new granules which might suggest that most of the structural changes occurring in new granules could be ascribed to changes occurring in starch molecules. Two endothermic peaks at 110° and 115°C in the thermograms of the old and new granules, respectively, coincide with loss of water.

At about 290°C combustion starts resulting in an exothermic peak at 312°C. Examination of the starch sample showed that these peaks correspond to a rapid physical expansion of the sample and not to any chemical property of the starch (Collison and Dickson, 1971). In view of this, the use of DTA thermograms as a "finger printing" device which has been suggested by Morita and Rice (1955), must be approached with caution. The endotherms at 160° and 165°C in the thermograms of old and new potato granules, respectively, correspond to the melting point of the monosaccharide glucose which is reported to be 165°C (Örsi, 1972 and Örsi, 1973). Decomposition of glucose begins at the melting point

and three reaction stages can be distinguished. The first decomposition stage begins on melting, and terminates at 240°C. Within this range two main processes occur. Firstly there is polymerization of part of the glucose with the formation of oligo- and polysaccharides. This process is accompanied by the formation of water, which evaporates at these temperatures. Secondly the residual glucose decomposes with the formation of some other unidentified substances, including brownish compounds. In the next decomposition stage, the brown compound and the accompanying polysaccharides might decompose and become insoluble. The peak at 290°C is common to both old and new granules and represents the beginning of the combustion of the sample which results in an exothermic peak at 312°C. The endothermic reactions of new granules at 365° and 400°C might be explained by further decomposition of the brown compounds and the accompanying polysaccharides formed in the earlier stages of the decomposition of glucose and sucrose.

It appears that the storage (ageing) of the granules brings about the structural changes among potato granules' main constituents. Since starch is main component of the granules, it is supposed that structural changes occurring within starch molecules initiate the changes to other constituents of the granules. This could be explained on the supposition that molecules of water which are usually inserted among starch molecules and kept in that position by H-bondings, leave their positions during ageing allowing starch molecules to come closer to each other. As a consequence of this would be the restricted penetration of water molecules into starch molecules, *i.e.* into the dry cells during rehydration. On the other hand, water being released from its previous positions could be picked up by other molecules

(proteins and pectic substances) causing their rearrangements too.

This analysis showed that the binding forces among molecules of old granules are stronger than the forces among molecules of new granules, the result of which is a reduced number of endothermic reactions in old granules.

No doubt this approach to the problem requires much more work to clarify the many questions concerning a very complex field of molecular rearrangements and interreactions which is beyond the scope of this thesis.

6.4.3.5. Effect of final drying temperature on rehydration of the granules

The effect of the final temperature of drying during processing of the potato granules by the F-T technique on the moisture content and rate of rehydration was observed. Table 10 shows the final drying temperature, and corresponding moisture content of the product, as well as the initial rate of rehydration of the granules. Figure 40 shows the rates of rehydration of these granules related to the final moisture content. The final moisture content of the granules was obtained by stopping the final process of drying when the temperature of the exhaust air in the fluidized-bed dryer reached 45°, 50°, 55° and 60°C. The rate of rehydration slows down as the final moisture content increases.

6.4.4. Remarks

6.4.4.1. Diffusivity

During processing of potato granules freezing, thawing and air drying with fluidization is applied. These treatments could

Table 10: Final Temperature of Drying and Corresponding Moisture Content and Rate of Rehydration of F-T Potato Granules

Final Temperature of Drying Air °C	Average Wet Basis Moisture Content of the Product in %	Rate of Rehydration kg water/ (kg wet material.s)
45	12.53	1.05×10^{-5}
50	8.44	1.15×10^{-5}
55	7.27	1.19×10^{-5}
60	5.48	1.79×10^{-5}

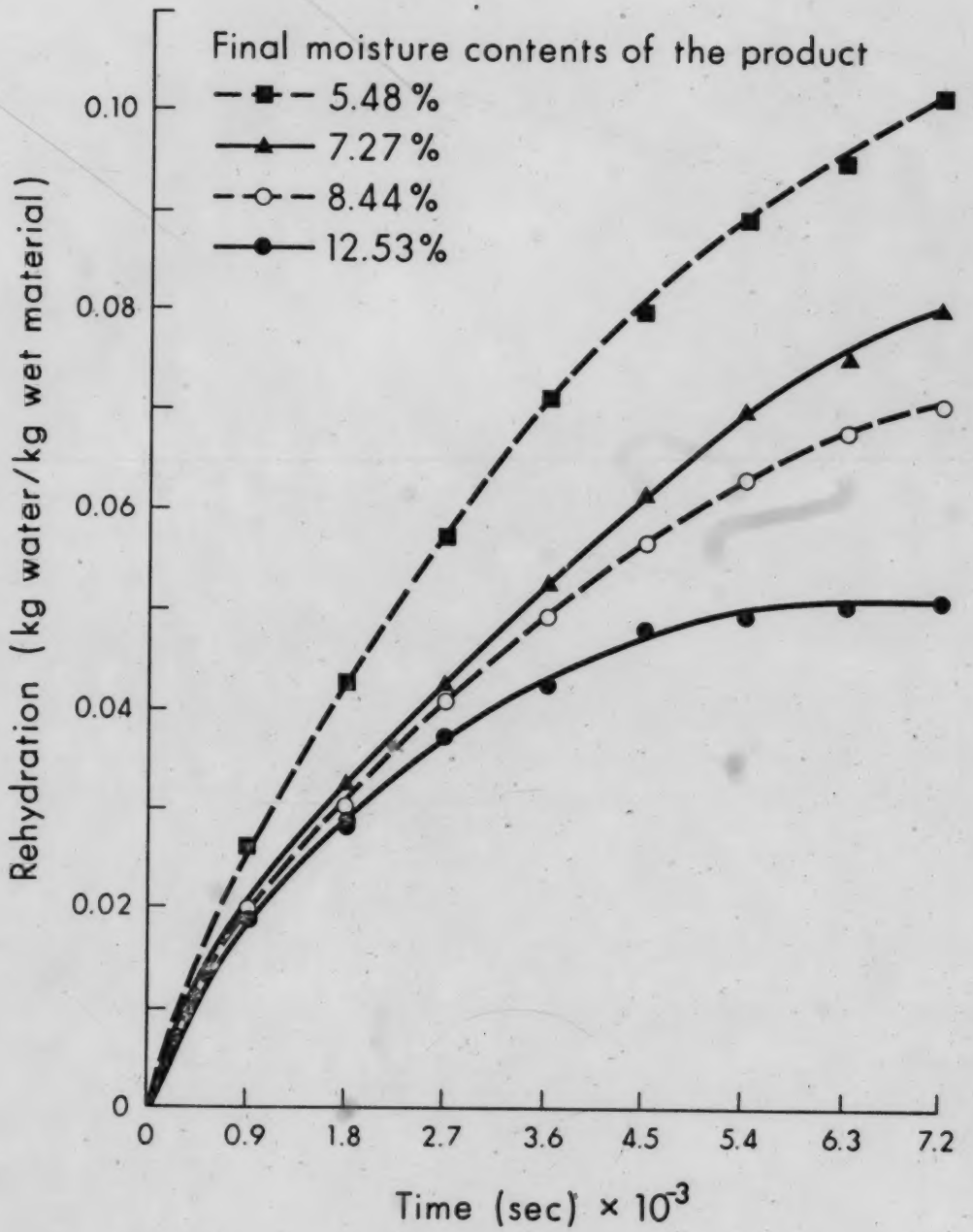


Figure 40. The relationship between rates of rehydration of the F-T granules and the final moisture content (as shown in Table 10).

significantly contribute to the structure of dehydrated potatoes (granules).

Saravacos (1967) considers air-dried potatoes compact in structure and freeze-dried potatoes very porous. Potato granules are porous although air dried, but with very small pores and sorption (diffusion) might be controlled by internal resistances to heat and mass transfer (King, 1968). During cooking, starch within the potato cells gelatinizes and looses its individuality filling all the interior of the cell. Under the microscope the cell reveals a continuous gel structure and exludes the possibility of the presence of pores. Due to the freezing as a further step in the processing of potato granules, small ice crystals form minute passages (pores) through the gel structure and through the cell wall. During further processing although reduced in size due to the shrinkage, the pores remain as a part of cell structure. However, the sorption studies showed that small pores ($R_p \simeq 6$ Å) are predominant and they could be too small to be able to let water molecules to penetrate into the granules. This leads to the hypothesis that rather than a pore phase diffusion, the sorption process of the F-T granules could be described as a solid phase diffusion in terms of an overall diffusion coefficient.

On the basis of the knowledge obtained by studying the surface structure of potato granules, sorption and diffusion characteristics of potato granules, it is possible to give a picture of what is actually happening during rehydration of the granules. Water penetrates freely through the fissures and grooves into the interior of the granule, covering internal surface. Further movement of water molecules slows down when the molecules "hit" the cell wall. However, due to the

presence of pits on the wall some water continues its path into the cell. Here, neglecting the presence of pores, the continuous starch gel structure resists water molecules movement. Water diffuses very slowly towards the center of the cell.

6.4.4.2. Influence of the water content on texture of rehydrated potato granules

Reconstituted doughs made from fresh and stored F-T granules using the previously described procedure, were submitted to an extrusion test. The extruded dough in the form of french fry made from the new F-T granules with an initial wet basis moisture content of 4.94% showed feathering on the edges of the strips. Besides, the french fry-form strips were very fragile and the cross-section showed non-uniform texture. The extruded dough made from the conditioned new F-T granules with an initial moisture content of 7.88% showed no feathering; the strips were firm and cross-sections showed uniform structure. From the previous results it is obvious that the water content of the granules is the critical factor in the making of the dough.

A simple mass balance shows that if m is the mass of granules used with an initial water content X_0, the mass of water M_w necessary to reach the optimum water content X_S is given by

$$M_w = \frac{m(X_S - X_0)}{1 + X_0} \qquad (6.10)$$

X_S corresponds to the water content of the dough which will give satisfactory results in the extrusion test. For fixed M_w and m (the case of industrial practice) the initial water content might play a critical role. A very dry initial product will lead to a lower water content of the dough. This is aggravated by the fact that at low water content the rehydration rate is fast and this will induce dry spots in

the dough.

6.4.4.3. Practical limitation of water content in the product

The above results show that the initial moisture content of the granules have an influence on rehydration chracteristics of the granules. As it was mentioned earlier it is important to know the optimum monolayer capacity of the product as well as the moisture content of the product above which the undesirable changes could take place most rapidly. Therefore, water content in the product should have a practical limit which however would give better rehydration property of potato granules. From the experiments, a suggested value of about 8% represents a reasonable compromise.

CONCLUSIONS

A rare appearance of pits on the surface of potato cells and aggregated potato cells in the form of the granules with many fissures, cracks and grooves are causing the surface of the granules, exposed to water during rehydration, to be quite large. As the result of this there exists relatively high possibility of an efficient rehydration. However, the experience shows that some batches of the same granules readsorb water faster leaving dry spots within the dough, and some re-adsorb water slower but uniformly giving the dough very uniform texture.

The experiments showed that the initial moisture content of the granules is responsible for the change of the rate of rehydration. If the granules have a low initial moisture content, there might exist quite a number of free -OH groups from the starch molecules on the surface of the granules (cells) as well as within the granules, in the pores. This is especially potentialized if the initial moisture content is less than the optimum monolayer capacity. During the rehydration the dipole molecules of water will quickly react with -OH groups from the starch on the surface of the granules. Further transport of water into the dry starchy material by the diffusion is aggrevated due to the loss of rotational freedom of the water molecules. Thermodynamically, the height of the energy barrier is increased due to the low initial water content (Fish, 1958). If the granules have a higher initial moisture content the outside surface and pore surface of the granules are covered with at least a layer of water molecules. During the rehydration there is no quick reaction (adsorption); a free

access of water into the dry starch gel is diminished. The critical radius (R_c) of some pores through which water could penetrate is reduced also. Therefore, the initial rate of rehydration is lowered. Due to the increase of rotational freedom of the water molecules, diffusion becomes greater and this causes better distribution of water through the granules, the result of which is the more uniform texture of the dough.

The study on diffusivity of the granules showed that rather than a pore phase diffusion, the sorption process of the F-T granules could be described as a solid phase diffusion in terms of an overall diffusion coefficient. Diffusion coefficients of potato granules although in agreement with the literature data for potato starch gel (10^{-13} m^2s^{-1}) (Fish, 1958) showed an insignificant change with the change of the initial moisture content of the granules. This, and the fact discovered by sorption studies that the granules are porous with the predominant presence of micropores, suggested the mechanism of diffusion of water into potato granules to be one of solid diffusion.

Sorption studies of the F-T potato granules enabled the author to calculate the optimum monolayer capacity, X_m = 5.42% (dry basis) (Table 2). This moisture content of the granules is almost always achieved in the final product by the standard procedure of the F-T process. It should be noted here that if processed granules have a lower water content, *i.e.* below the monolayer capacity, this would have a consequence on the characteristics of the product. The water molecules of monolayer have a protective effect due to retardation of oxygen diffusion. They could also coordinate trace metals and reduce their catalytic effect or possibly decompose free radicals (Salwin,

1963) and therefore, the result of this is oxidation and catalytic reactions detrimental to the product. Moisture in excess of the monolayer value could promote browning, hydrolysis, caking and other effects. These undesirable changes take place most rapidly at a water activity above the range of a_w = 0.50 to 0.65 (Labuza, 1970), which for F-T potato granules corresponds to moisture content somewhere above 9.9% (11.0 kg water/100 kg dry solids) (Table 7). At higher values bacteria and food spoilage organisms would appear (Bone, 1973). This is very important to be aware of, since in this study a compromise has been found between the two limits (5.42% and 11.00%, dry basis) and a value of about 8% was suggested. This value insures desirable rehydration properties of the granules; it does not induce the spoilage and consequently reduces the processing time. To achieve this, three possibilities to improve the product could be suggested:

1. Standardization of the processing conditions to achieve a product of constant characteristics (*i.e.* to stop the process of drying when the final temperature of exhaust air reaches 55°C) (Fig. 40 and Table 10).
2. If the above solution is difficult to realize because of raw material variations, the processed granules should be exposed to standard storage conditions (RH and Temperature) to ensure the same water content and reproducibility of dough making (Table 7).
3. The existing ratio for making the french fry dough (water: granules ≈ 2:1) should be corrected to its exact value after analysis of the water content, if none of the two preceeding steps are possible.

It appears that the initial moisture content is not the only parameter responsible for the change of the rate of rehydration of potato granules. The experiments conducted excluding the possibility of the alteration of the moisture content, showed the change of rehydration properties of the granules when they were stored for a longer time (up to 60 days). Molecular rearrangement within potato granules is believed to be the cause of this. The thermograms obtained by differential thermal analysis of new and one year old F-T potato granules are used to support the above statement. The results on rehydration of the granules obtained in these experiments cannot be considered of an industrial importance. In the case where the granules were stored under the $a_w = 0$, moisture content is far below the optimum monolayer capacity and the slowdown in the rate of rehydration is not significant. In the second case (storage under the $a_w = 0.518$), although the rate of rehydration is satisfactory, the moisture content is high and over the desirable optimum which would give a dough of constant and optimum quality for the making of french fries.

Finally, in both cases the changes are rather slow which would create an economical problem if this happens to be a method for improving rehydration properties of the granules. However, the time factor plays an important role and there exists evidence for the molecular rearrangements within the granules.

From the industrial point of view, it is believed that the results from this work will contribute to the solving of existing problems of the inconsistent rehydration rate of potato granules.

Looking at this work from the scientific corner, it remains yet to give some answers concerning molecular rearrangements. The questions

to be answered are:

1. To what extent and in what way are starch, pectin and protein molecules involved in molecular rearrangement (mechanism)?
2. Is it possible to increase the rate of these changes?
3. Does any organoleptic change exist in reconstituted products which would be considered undesirable?

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APPENDIX: Excerpt from the computer print-out. Data on desorption of new F-T potato granules and their corresponding parameters.

NEW POTATO GRANULES (FREEZE-THAW TECHNIQUE)

1 P/PO	2 W	3 WM A	4 T	5 DM A	6 MPOAM A	7 MADAM A	8 DT A	9 DV	10 DWT	11 DWM	12 DWP	13 DSP M/PO	14 S M/PO	15	16 MET PROT
.720	17.4	32.8	5.0	37.1	37.4	32.4	.035	.143	.014	.137	.173	.91	38.7	.738	
.715	17.2	31.4	5.0	36.4	36.7	31.7	.035	.140	.014	.126	.169	.90	39.6	.737	
.710	17.1	30.7	5.0	35.7	36.0	31.1	.034	.137	.014	.123	.165	.90	40.5	.735	
.705	16.9	30.1	4.9	35.1	35.4	30.6	.034	.133	.014	.120	.162	.91	41.5	.732	
.700	16.8	29.5	4.9	34.4	34.7	29.9	.033	.130	.014	.115	.158	.91	42.4	.729	
.695	16.7	28.9	4.9	33.8	34.1	29.2	.032	.127	.014	.113	.154	.90	43.3	.727	
.690	16.6	28.4	4.8	33.2	33.5	28.7	.032	.124	.014	.110	.151	.90	44.2	.725	
.685	16.4	27.8	4.8	32.6	32.9	28.1	.031	.122	.014	.104	.148	.90	45.1	.722	
.680	16.3	27.3	4.8	32.1	32.4	27.6	.031	.119	.014	.105	.144	.89	46.0	.720	
.675	16.2	26.8	4.7	31.5	31.8	27.0	.030	.116	.014	.102	.141	.89	46.9	.718	
.670	16.1	26.3	4.7	31.0	31.3	26.5	.030	.114	.014	.100	.138	.88	47.7	.715	
.665	16.0	25.8	4.7	30.5	30.7	26.1	.029	.111	.014	.097	.135	.88	48.6	.713	
.660	15.9	25.3	4.7	30.0	30.2	25.6	.029	.109	.014	.095	.133	.88	49.5	.711	
.655	15.8	24.9	4.6	29.5	29.8	25.1	.028	.107	.014	.093	.130	.87	50.4	.709	
.650	15.7	24.4	4.6	29.0	29.3	24.7	.028	.106	.014	.092	.127	.87	51.2	.707	
.645	15.6	24.0	4.6	28.6	28.8	24.2	.027	.102	.014	.088	.125	.87	52.1	.704	
.640	15.5	23.6	4.5	28.1	28.4	23.8	.027	.101	.014	.086	.123	.86	53.0	.702	
.635	15.4	23.2	4.5	27.7	27.9	23.4	.026	.099	.014	.085	.120	.86	53.9	.700	
.630	15.3	22.8	4.5	27.3	27.5	23.0	.026	.097	.014	.083	.118	.86	54.7	.698	
.625	15.2	22.4	4.5	26.9	27.1	22.6	.026	.095	.014	.081	.116	.86	55.6	.696	
.620	15.1	22.0	4.4	26.5	26.7	22.2	.025	.094	.014	.080	.115	.86	56.4	.694	
.615	15.0	21.7	4.4	26.1	26.3	21.8	.025	.092	.014	.079	.113	.85	57.3	.692	
.610	14.9	21.3	4.4	25.7	25.9	21.5	.024	.091	.014	.077	.111	.85	58.1	.690	
.605	14.8	21.0	4.4	25.3	25.5	21.1	.024	.090	.014	.076	.110	.85	59.0	.688	
.600	14.7	20.6	4.3	25.0	25.1	20.8	.024	.089	.014	.076	.109	.87	59.9	.685	
.595	14.6	20.3	4.3	24.6	24.8	20.4	.023	.088	.014	.075	.107	.87	60.7	.683	
.590	14.5	20.0	4.3	24.3	24.4	20.1	.023	.087	.014	.072	.107	.87	61.6	.681	
.585	14.4	19.6	4.3	23.9	24.1	19.8	.023	.086	.014	.071	.106	.88	62.5	.678	
.580	14.4	19.3	4.3	23.6	23.7	19.5	.023	.085	.014	.071	.105	.88	63.4	.676	
.575	14.3	19.0	4.2	23.3	23.4	19.2	.022	.084	.014	.070	.104	.89	64.3	.674	
.570	14.2	18.7	4.2	22.9	23.1	18.9	.022	.084	.014	.070	.104	.90	65.2	.672	
.565	14.1	18.4	4.2	22.6	22.8	18.6	.022	.083	.014	.069	.104	.91	66.1	.670	
.560	14.0	18.2	4.2	22.3	22.5	18.3	.021	.083	.014	.069	.104	.92	67.0	.667	
.555	13.9	17.9	4.1	22.0	22.2	18.0	.021	.083	.014	.068	.104	.93	67.9	.664	
.550	13.9	17.6	4.1	21.7	21.9	17.7	.021	.083	.014	.068	.104	.95	68.9	.662	
.545	13.8	17.3	4.1	21.4	21.6	17.5	.021	.083	.014	.068	.104	.96	69.8	.659	
.540	13.7	17.1	4.1	21.2	21.3	17.2	.021	.083	.015	.068	.104	.98	70.8	.656	
.535	13.6	16.8	4.1	20.9	21.0	17.0	.020	.083	.015	.068	.105	1.00	71.8	.653	
.530	13.5	16.6	4.0	20.6	20.8	16.7	.020	.083	.015	.068	.106	1.02	72.8	.650	
.525	13.4	16.3	4.0	20.4	20.5	16.5	.020	.083	.015	.069	.106	1.04	73.9	.647	
.520	13.4	16.1	4.0	20.1	20.2	16.2	.020	.084	.015	.069	.107	1.06	74.9	.644	
.515	13.3	15.9	4.0	19.8	20.0	16.0	.020	.084	.015	.070	.107	1.09	76.0	.641	
.510	13.2	15.6	4.0	19.6	19.7	15.8	.019	.085	.015	.070	.108	1.11	77.1	.637	
.505	13.1	15.4	3.9	19.4	19.5	15.5	.019	.085	.015	.071	.111	1.14	78.3	.634	
.500	13.0	15.2	3.9	19.1	19.2	15.3	.019	.086	.015	.071	.112	1.16	79.4	.631	
.495	12.9	15.0	3.9	18.9	19.0	15.1	.019	.086	.015	.071	.113	1.19	80.6	.627	
.490	12.9	14.8	3.9	18.6	18.8	14.9	.019	.086	.015	.071	.113	1.21	81.8	.624	
.485	12.8	14.5	3.9	18.4	18.5	14.7	.018	.086	.015	.071	.114	1.23	83.1	.620	
.480	12.7	14.3	3.8	18.2	18.3	14.6	.018	.086	.015	.071	.114	1.25	84.3	.616	
.475	12.6	14.1	3.8	18.0	18.1	14.2	.018	.086	.015	.071	.115	1.27	85.6	.612	
.470	12.5	13.9	3.8	17.8	17.9	14.0	.018	.086	.015	.071	.115	1.28	86.9	.608	
.465	12.4	13.8	3.8	17.6	17.7	13.8	.018	.086	.015	.071	.115	1.30	88.2	.604	
.460	12.3	13.6	3.8	17.3	17.4	13.7	.018	.086	.015	.07	.115	1.31	89.5	.599	
.455	12.2	13.4	3.8	17.1	17.2	13.5	.018	.086	.015	.071	.115	1.33	90.9	.595	
.450	12.2	13.2	3.7	16.9	17.0	13.3	.017	.085	.015	.071	.115	1.34	92.1	.590	